CONSTITUTION OF OIL-SHALE KEROGEN: BIBLIOGRAPHY AND NOTES ON BUREAU OF MINES RESEARCH

By W. E. Robinson and K. E. Stanfield

* * * * * * * * * * * information circular 7968

March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

This publication has been cataloged as follows:

Robinson, Wilbur Eugene

Constitution of oil-shale kerogen: bibliography and notes on Bureau of Mines research, by W. E. Robinson and K. E. Stanfield. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1960]

79 p. 27 cm. (U.S. Bureau of Mines. Information circular 7968)

Based on work done under cooperative agreement between the Bureau of Mines and the University of Wyoming.

1. Oil-Shales - Bibl. 2. Kerogen - Bibl. I. Stanfield, Kenneth Edison, joint author. II. Title. (Series)

TN23.U71 no. 7968 622.06173

U.S. Dept. of the Int. Library

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Washington 25, D.C. - Price 45 cents

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CONSTITUTION OF OIL-SHALE KEROGEN: BIBLIOGRAPHY AND NOTES ON BUREAU OF MINES RESEARCH[1]

by

W. E. Robinson[2] and K. E. Stanfield[2]

INTRODUCTION

Oil-shale kerogen was processed into oil and oil products before the first oil well was completed by Drake in 1859. However, because of economic and other advantages, natural petroleum has been the principal source of liquid fuels and lubricants since 1859 and is a convenient root of many organic chemicals in common use today.

In recent years the difference has narrowed between the cost of producing liquid fuels from well petroleum and other sources. This narrowing of cost difference has resulted both from the increased cost of finding new sources of petroleum in the United States and the experimental demonstration of lowered costs for synthetic liquid fuels by the Federal Bureau of Mines and by industry. Available petroleum resources of this country are being reduced and eventually may be inadequate to meet the demand. Alternate means of assuring an adequate supply of liquid fuels for this country include the development of processes for utilizing other carbonaceous materials such as oil shale and coal.

Large deposits of oil shale potentially suitable for commercial development exist in the Green River formation. According to Duncan[3], the Piceance Creek basin in Colorado has about 3 trillion tons of shale in place with an oil yield of more than 1 trillion barrels. Less information is available for the Uinta basin in Utah and the Green River basin in Wyoming. However, rough calculations indicate the former has about 200 billion tons of oil shale with an estimated oil yield of about 120 billion barrels, and the Green River basin of Wyoming has approximately 20 billion tons of shale with an oil yield of about 12 billion barrels. Duncan estimated that the oil shale in the Green River formation that may be suitable for commercial development represents a total of about 1-1/8 trillion barrels of oil.

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[3] Duncan, Donald C., Oil-Shale Deposits in the United States: Independent Petrol. Assoc. of America, vol. 29, No. 4, 1958, pp. 22, 49-51.

Basic research on the structure of kerogen and processes by which it is degraded to useful products is needed to aid the development of new and better methods of using oil shale. At present government laboratories, educational institutions, and private laboratories are studying these problems, but progress on this research is slow. Consequently, only a limited number of studies of this nature are described in the literature.

The purpose of preparing these abstracts was to assemble the important data published through 1957 about the constitution of kerogen. The study of the structure of kerogen is closely related to studies of origin and geology of oil shale, composition and properties of the inorganic part of oil shale, and composition of shale oil. Publications of this nature contributing to the knowledge of the structure of kerogen have been included. The authors believe that these abstracts will help to correlate the available information and will be useful in future research on the constitution of kerogen.

References to articles included in this report were obtained largely from the following sources:

1. Analytical Chemistry

2. Beacon Laboratory, Oil Shale, The Texas Co., Beacon, N. Y., 1948, 764 pp.

3. Chemical Abstracts

4. Industrial and Engineering Chemistry

5. Industrial Arts Index

6. Journal of the American Chemical Society

7. McKee, Ralph H., Shale Oil, The Chemical Catalog Co., New York, N. Y., 1925, 326 pp.

8. Oil and Gas Journal

9. The Institute of Petroleum, Oil Shale and Cannel Coal. The Institute of Petroleum, London, England, 1938, 473 pp.; vol. 2, 1951, 832 pp.

10. Federal Bureau of Mines publications

11. Miscellaneous reports

Information in this report concerns: (1) Abstracts of published articles organized into four major sections and several subsections based on subject matter. These abstracts are arranged according to date of publication. (2) A miscellaneous bibliography for each major section of abstracts. The bibliography is arranged alphabetically according to the first author named on each citation. (3) A final section comprised of notes on unpublished research performed by the Bureau of Mines at its Laramie Petroleum Research Center, Laramie, Wyo. The notes are arranged under the same subjects used for the abstracts. Each item is assigned an identification number. Arabic numerals refer to the abstracts and bibliographies. Roman numerals refer to notes on unpublished research of the Bureau of Mines. These identification numbers are used in the subject and author indices at the end of the report.

Some of the abstracted articles are controversial. The authors have tried to abstract the information impartially and assume no responsibility for the authenticity of the conclusions presented. In instances of errors, the authors have called attention to these as "author notations." Most of the abstracts were made from original publications or translations. A few abstracts of foreign articles were taken from "Chemical Abstracts," and appropriate notations were made.

FORMATION OF OIL SHALE[4]

Geology[5]

1. WINCHESTER, DEAN E. Oil Shale of the Uinta Basin, Northeastern Utah. Geol. Survey Bull. 691(b), 1918, pp. 27-50.

The Tertiary rocks, which occupy the interior of the Uinta basin, have been subdivided into four formations--Wasatch, Green River, Bridger, and Uinta. The division is based on stratigraphic and paleontologic evidence. The Wasatch, oldest of these formations, consists of coarse sandstones, highly colored shales, and thin lenses of coal. The Green River, which contains oil shales, overlies the Wasatch and underlies the Bridger. It includes evenly and thinly bedded gray and white calcareous shale, with some sandstone, oolite, and limestone. The Bridger and Uinta formations are composed of irregularly bedded clay shale and ferruginous sandstone, and are distinguished from each other largely by their different fossil content. Each formation is very fossiliferous.

Hydrocarbon materials have been found in all four formations, although bedded deposits (asphaltic sandstone and oil shale) are known only in the Wasatch and Green River. Veins of gilsonite, elaterite, ozocerite, and other related hydrocarbons cut all the Tertiary formation of the Uinta basin.

Good oil shale (Uinta basin of Utah) is black or brownish black except on weathered surfaces, where it is blue-white or white. It is fine grained, slightly calcareous, and usually free from grit. It is tough and in thin-bedded deposits remarkably flexible. The flexibility of oil shale distinguishes it from ordinary carbonaceous shale, which is brittle. Although oil shale consists of thin laminae, this is not apparent in some specimens until after the rock has been heated and the oil driven off. Freshly broken oil shale gives off a peculiar odor similar to that of crude petroleum, although the shale contains little oil or bituminous matter that is soluble in ether,

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[4] Titles in parentheses are translations from the language in which the item was published.

[5] Additional information is presented in item 20.

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chloroform, carbon disulfide, or other solvents of bitumen. Oil shale contains a large amount of carbonaceous matter (largely remains of lower plants, including algae), which is the source of the distillation products. Thin splinters of oil shale will burn with a very sooty flame and give off an asphaltic odor. Lean specimens of oil shale have a higher specific gravity than rich specimens and are generally heavier than coal.

Notes by C. A. Davis, dated Oct. 30, 1914: Oil shale is composed of organic, bituminous, and mineral matter. Rich shales are compact and impervious, and appear to be composed of partly decomposed plant algae, fungi, spores, pollens, and bacteria. This material was embedded as a jellylike mass, which contained few if any interspaces. It appeared improbable that the bituminous matter present in oil shale migrated into the shale bed because of physical characteristics of the deposit. It is more likely that the bituminous matter originated in the highly organic bed.

2. GEORGE, R. D. Oil Shale in Colorado. I. Railroad Red Book, vol. 38, 1921, pp. 457-461.

Mountain-making movements at the close of the Cretaceous and opening of the Tertiary times caused the formation of a great basinlike depression occupying the northwest corner of Colorado, the southwest quarter of Wyoming, and the northeast corner of Utah. This depression was approximately 300 miles from north to south and 200 miles from east to west. Drainage from the surrounding country poured into this great basin, forming a lake nearly twice the area of Lake Superior. (Author's note. - The present concept is that, although contemporaneous, the Green River formation in Wyoming and that in the Sand Wash basin of Colorado were originally deposited in ancient Lake Gosiute. The Green River formation of Utah and the remainder in Colorado were deposited in ancient Lake Uinta.)

The Uinta mountain fold almost divides the southern one-third of the lake from the northern two-thirds, but the same conditions of deposition prevailed north and south of the ridge. Streams flowing into the lake carried vast quantities of sediment from the surrounding country, and waves spread this material rather uniformly over the floor of the lake. This formed four great Eocene rock series--the Wasatch, Green River, Bridger, and Uinta--having a total thickness of several thousand feet. In a gradual filling of the basin with sediment and deepening of the valley of the Green River caused the disappearance of the lake and formation of soft sedimentary rocks, consisting mainly of shales, a small percentage of sandstone, and a still smaller proportion of limestone. On this new surface, rivers and their tributaries carved the present topography, of which the main features are broad mesas or plateaus deeply cut by canyons and broadened by steep slopes and cliffs. Most of the strata of these Tertiary formations still lie in a horizontal position, but occasionally they are tilted at angles as great as 20°. Of these four rock series, the second from the bottom (the Green River) contains the oil shales, which occur mainly in the upper half of this formation.

3. BARB, CLARK F. Review of Geology and Field Work. Colorado Sch. Mines Quart., vol. 39, No. 1, 1944, pp. 7-65.

The carbonaceous materials of the Uinta basin are interesting and unique. They include gilsonite (uintaite), wurtzilite, ozocerite, tabbyite, albertite (nigrite), native asphalt, oil shale, glance pitch, natural gas, coal, and crude petroleum.

The Uinta basin has been described as a topographic as well as a structural basin. When viewed from one of the cliffs on the south edge of the Uinta mountains, nearly the entire basin can be seen as outlined by its natural boundaries. The basin is usually described as being bounded on the north by the east-west range of the Uinta mountains, on the south by the east-west horizon of the Roan or Brown cliffs, on the west by the passes of the Wasatch mountains, and on the east by the rimrocks of the Rangely dome and the Grand Hogback. The basin is approximately 175 miles from east to west, 40 to 120 miles from north to south, and covers an area of about 8,000 square miles in Utah and about 7,000 square miles in Colorado. The surface geology of the basin is characterized by Tertiary deposits, although Upper Cretaceous and older beds have been exposed in the stream valleys or on the flanks of the boundary uplifts. The Tertiary formations, with a total thickness of 500 to 12,000 feet, seem to lie unconformably on an eroded Cretaceous surface all over the basin. In some areas the Upper Tertiary may lie unconformably on Lower Tertiary beds.

Except for coal, the many carbonaceous materials of the Uinta basin occur only in the Tertiary formation and appear to have a common relationship. Among their common characteristics are a peculiar tacky feel, a rubbery odor when burned, and a peculiar resistance to atmospheric oxidation exhibited by both solid and liquids from some deposits.

Theories of Origin[6]

4. STEUART, D. R. The Oil Shales of the Lothians, Part III, The Chemistry of the Oil Shales. Mem. Geol. Survey, Great Britain, Scotland, 1912, pp. 163-166.

Tests were performed whereby fuller's earth and lycopodium spore dust were heated to retorting temperatures and the crude oil examined. Oil shale may be composed of the following: Vegetable matter that has been macerated and preserved by combining with salts, spores, and other such material that has been protected from decay, and a proportion of animal matter. Generally, oil shale may be considered as a torbanite that contains a large proportion of inorganic matter, or it may be a torbanite that has deteriorated with age. This supposition is based on the fact that oil yield decreases and the yield of ammonia increases with age.

5. CUNNINGHAM-CRAIG, E. H. The Origin of Oil Shale. Proc. Roy. Soc. (Edinburgh), vol. 36, 1915, pp. 44-86.

Kerogen was believed to be formed by the inspissation of petroleum. During this process nitrogen and sulfur compounds were concentrated in the most inspissated or weathered products. At a certain stage, reached gradually, the organic matter became insoluble in carbon-disulfide and ceased to be a bitumen. Oil shale was formed by the power of certain clays or shales to absorb inspissated petroleum, particularly unsaturated hydrocarbons. This adsorption apparently depended on the colloid content of the argillaceous rock. This rock retained these impregnated petroleum residues long after porous sandstones in the vicinity had lost all traces of petroleum by weathering and leaching.

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[6] Additional information is presented in items 1, 48, 49, 64, 105, and 108.

6. CONACHER, H. R. J. The Origin of Scottish Oil Shales. Petrol. Rev., December 1916, p. 509.

Oil shales contain two distinct types of organic material, one is comparable to the woody material in coal and the other consists of yellow bodies. When distilled, the latter yields the liquid product typical of oil shale, whereas the woody material produces large amounts of ammonia. The yellow bodies have been described by various investigators as fossil algae, spores, or dried-up globules of petroleum. In this study it was concluded that the yellow bodies were fragments of resins set free by the decay and oxidation of the vegetable matter with which they were originally associated.

7. BISHOP, JAMES A. How Oil Is Manufactured in Nature's Laboratory. Salt Lake Mining Rev., vol. 22, 1920, pp. 27-32.

The production of hydrocarbonlike material from cellulose and protein may be accounted for in the following manner: Large masses of plant and animal tissue accumulated as debris and submerged quickly in muddy waters. A water seal may have been formed against the admission of atmospheric oxygen, and the organic material was not completely converted to carbon dioxide, water, and ammonia. No organic compound contains sufficient oxygen to completely oxidize the elements of its own composition. Hence, if oxidation of any organic compound be restricted to the oxygen within itself, there must remain a hydrocarbon residue. Differences in animal and vegetable life in various locations caused variations in the composition of the organic matter present in oil shales.

8. SCOTT, JAMES. Petroleum Under the Microscope. Petrol. World, vol. 17, 1920, pp. 300, 346-347, 385-387.

Kerogen may have been formed by a gradual change of vegetable matter into kerogen globules that were intimately mixed with clay and other minerals. As these globules accumulated, the more volatile constituents were eliminated, leaving the remainder as a heavy residue. This process is termed inspissation.

9. GEORGE, R. D. Oil Shale in Colorado. II. Railroad Red Book, vol. 38, 1921, pp. 521-525.

Oil shale contains no hydrocarbon liquids at atmospheric temperature. Solid hydrocarbons occur in minute particles and in widely differing quantities, but there seemed to be no direct relationship between the oil yield and the presence of these hydrocarbons. The shales contain partly bituminized vegetable matter (possibly some animal matter), and the quantity of this material plus hydrocarbons determines the oil yield. The degree of bituminization of the vegetable matter differs from place to place and from stratum to stratum. This change in the vegetable matter is comparable to the evolution of coal from plant matter. The oil-yielding materials of shale are related to lignite or coal on the one hand and to true hydrocarbons on the other. The closeness of the relationship depends upon the nature and degree of alteration of the vegetable matter in the shale.

10. HACKFORD, J. E. The Chemical Aspects of Shale and Shale Oils. Oil Eng. Finance, vol. 1, 1922, pp. 659-662, 813-815.

To prove that the kerogen in oil shale is a form of bitumen, several experiments were made with oil shale and a heavy asphaltic oil mixed with fuller's earth. When distilled, both the oil shale and asphalt-impregnated fuller's earth yielded paraffin oil, wax, and hydrogen sulfide (if sulfur was present). Both yielded ammonia if nitrogen was present. The organic material in each was partly isolated by extraction with pyridine and appeared to be the same. Oil shale is a marl that was saturated with oil or through which oil has passed or filtered. The insolubilities of its organic compounds are due to a slightly elevated temperature for a prolonged period and to the retaining effect exerted by the finely divided marl. The marl exerted a selective action on the oil and absorbed the asphaltum, sulfur, and nitrogen compounds from the oil. The class of oil evolved from a shale depended on the nature of the original compounds absorbed. Asphaltenes obtained from crude oil by precipitation with ethyl ether produced distillation products of water, hydrogen sulfide, ammonia, oil, wax, and a carbonaceous residue. Water was formed by decomposition of oxyasphaltenes and hydrogen sulfide by decomposition of thioasphaltenes. Ammonia was evolved during decomposition if lime was present, but if there was not sufficient free lime present, pyridine and pyrrole derivatives were redistilled as such. The oil and wax that resulted from the dry distillation were true decomposition products and equaled about 60 weight-percent of the asphaltenes. The oil and wax content of the mixture varied between 8 and 10 percent. The carbonaceous residue, which represented approximately 40 percent of the original asphaltene, was a decomposition product of the asphaltenes. Geologic comparisons of oil-shale deposits and oil-well fields were also made.

11. RAE, COLIN C. Organic Material of Carbonaceous Shales. Bull. Am. Assoc. Petrol. Geol., vol. 6, 1922, pp. 333-341.

Microscopic examinations of shales associated with oil showed the presence of an ulmohumic groundmass plus other identifiable organic remains. Asphalt may be formed from the ulmohumic acid precipitates in the presence of sea water and electrolytes. Rivers and streams acted as concentrating agents for millions of tons of organic materials, which later were incorporated into marine or inland lake deposits. Heat, pressure, and catalytic agents converted the organic material to petroleum.

12. JONES, J. CLAUDE. Suggestive Evidence on the Origin of Petroleum and Oil Shale. Oil Eng. Finance, vol. 3, 1923, pp. 443-444, 452.

Oil shales and coals originated in fresh water muds that contained large amounts of spores, algae, and other nonwoody vegetable material. This organic debris was partly decomposed by bacterial action but not enough to increase the percentage of fats by removal of other plant substances. By contract, petroleum was formed by thorough decomposition of nonfatty material in salt water. The main difference in bacterial action was due to differences in the saline content of the water in which the organic material was deposited. In fresh water, the amount of decay was small, whereas in salt water it was nearly complete.

13. WEEKS, W. G. The Origin of Oil Shales. Oil Eng. Finance, vol. 3, 1923, pp. 643-644.

The theory by Jones was questioned. Oil shales do not contain partly decomposed vegetable matter, and, where particles of vegetation are identified, they do not prove that kerogen was formed in its place. Some shales do contain free oil that can be extracted with solvents.

14. TRAGER, E. A. Kerogen and Its Relation to the Origin of Oil. Bull. Am. Assoc. Petrol. Geol., vol. 8, 1924, pp. 301-311.

Cylinders of oil shale (author's note, probably from DeBeque, Colo.), 1/2 inch in diameter by 1-1/2 inches long, were placed in a steel cylinder resembling a spool, and sufficient pressure was applied by a plunger to bulge the wall of the cylinder. The cylinder then was sawed open, and the shale examined. Samples of oil shale also were heated and then examined under a microscope.

Kerogen, before being subjected to high temperatures or pressures, is brown to dark orange in color and is optically inactive. When heated to a temperature slightly less than the temperature of vaporization and then allowed to cool, kerogen yields a vitreous, lemon-colored anisotropic substance. Kerogen can also be converted into oil, either by the aid of heat or by pressure; but in the latter instance the pressure must be of such nature to allow molecular displacement.

15. VAN TUYL, F. M., AND BLACKBURN, C. O. The Effect of Rock Flowage on the Kerogen of Oil Shale. Bull. Am. Assoc. Petrol. Geol., vol. 9, 1925, pp. 158-164.

Oil-shale samples from Grand Valley, Colo., and Elko, Nev., were placed in spoollike cylinders, 1/2-inch in diameter and 2 inches in length. The shale cylinders were subjected to increasing increments of pressure until the thin walls of the spool bulged. The treated shale sample was then extracted for 3 hours with chloroform, and the percent soluble bitumen determined.

Failure to produce free oil during the flowage of oil shale in the above experiments raised a doubt as to whether the shale used by Trager was a true oil shale.

The above experiments showed that free oil was not formed from kerogen at elevated pressures and ordinary temperatures, however, the original source material of both kerogen and petroleum may have been similar in character. Details of the transformation of the source material into these substances may have been different.

16. _____. The Relation of Oil Shale to Petroleum. Bull. Am. Assoc. Petrol. Geol., vol. 9, 1925, pp. 1127-1142.

Samples of oil shale from DeBeque (Colo.) were subjected to pressures of 23,979 p.s.i. for a total of 2-1/3 hours at 100° C. It was impossible to produce free oil from kerogen by subjecting them to the above pressure at room temperature or at elevated temperatures, equivalent to those that normally exist at a depth of more than 8,000 feet in the earth's crust. Therefore, important quantities of petroleum could not have been formed from oil shale in nature except in the vicinity of igneous intrusions where temperatures had been unusually high.

Kerogen and petroleum are not genetically related but represent different end products of the transformation of organic debris. Differences in bacterial action at the time of deposition and other causes were important in determining the character of the final product obtained.

17. McKEE, RALPH H., AND MANNING, PAUL D. V. Shale Oil. I. The Genesis of Oil Shales and Its Relation to Petroleum and Other Fuels. Oil Bull., vol. 13, 1927, pp. 65-69, 175-181, 291-301.

Oil-shale kerogen originated from resinous vegetation residues of past eras, whereas well petroleum was formed from oil shales by pressure and mild heat. Petroleum migrated to its present reservoir from neighboring oil-shale deposits, leaving a residue of black bituminous shales. The high carbon dioxide content of gases present in petroleum wells originated from kerogen, as it gives off carbon dioxide gas before producing soluble oil or bitumen.

18. HAWLEY, J. E. Generation of Oil in Rocks by Shearing Pressures. II. Effect of Shearing Pressures on Oil Shales and Oil Bearing Rocks. Bull. Am. Assoc. Petrol. Geol., vol. 13, 1929, pp. 329-366.

Colorado, Australian, Kentucky, and Ohio oil shales were subjected to high shearing pressures of various intensities under different conditions so that they yielded from fracture or by flow. All shearing-pressure tests conducted at room temperature on various oil shales failed to generate oil. The pressure exerted ranged from 38,000 to more than 100,000 p.s.i.

19. STADNICHENKO, TAISIA, AND WHITE, DAVID. Microthermal Studies of Some "Mother Rock" of Petroleum from Alaska. Bull. Am. Assoc. Petrol. Geol., vol. 13, 1929, pp. 823-840.

Oil is derived from a portion of oil-shale kerogen and not from the entire mass. Kerogen is not a pure chemical constituent, and the oil produced from it is different from the originating material. Differences in the melting points and in the behavior of the groundmass in advanced stages of carbonization confirm these findings.

20. BRADLEY, WILMOT H. Origin and Microfossils of the Oil Shale of the Green River Formation of Colorado and Utah. Geol. Survey Prof. Paper 168, 1931, 58 pp.

The Green River formation of Colorado and Utah is a series of lakebeds of middle Eocene age that occupy two broad, shallow, simple, structural basins--the Piceance Creek basin in northwestern Colorado and the Uinta basin in northeastern Utah. The ancient lakes served as a basin for the accumulation of tremendous quantities of aquatic organisms. The predominance of microscopic fresh-water algae and protozoa over the remains of land plants, pollens and spores, suggests that the greater part of the organic matter was derived from microorganisms that grew in the lakes. The pollens and spores were carried into the lakes by wind. Fish, mollusks, crustaceans, and aquatic insect larvae were also plentiful; and turtles, crocodiles, birds, small camels, and insects may have contributed to the organic matter.

The ancient lakes apparently were shallow and had a large area, compared with depth. The abundance of organisms and the decaying organic matter produced a strongly reducing environment. Mechanical and chemical action, such as the mastication and digestion of the organic material by bottom-living organisms, caused disintegration of the original organic matter. When the residue was reduced to a gelatinous condition, it apparently resisted further bacterial decay, and other organisms accidently entombed in the gel were protected from disintegration. An accumulation of inorganic material occurred simultaneously with the disintegration of the organic ooze, and the entire mass became lithified. After most of the oil shale was deposited, the lake reverted nearly to the conditions that prevailed during its early stage, when the marlstone and low-grade oil shale of the basal member were formed. The streams in the vicinity of the lake were rejuvenated and carried great quantities of medium- to coarse-grained sand into the basin and formed a thick layer over the lakebeds.

Microgranular calcite and dolomite are the predominant mineral constituents of most of the oil shale. Analcite is plentiful; quartz, sanidine, orthoclase, plagioclase, muscovite, hornblende, pyroxene, zircon, apatite, opal, and bits of volcanic glass are present in smaller amounts. Pyrite is abundant in most beds and indicates that the original organic ooze was a strongly reducing medium.

The microflora of the Green River formation consist of two forms that have been referred to as bacteria and many fungi spores. Of the algae--all microscopic--one flagellate, a naked protoplast, five blue-green algae, and five green algae were found; no diatoms were evident. Of the higher plants, spores and pollens were plentiful; eight spores and nine different pollens were observed. A fragment of bark, a part of a spiral tracheid, and a few stellate hairs are the only parts of the tissues of plants higher than mosses and ferns that have been found. The fauna include rhizopods, insects, and a mite.

Two kinds of organic matter are seen in thin sections of the oil shale; one is massive and structureless and is the matrix of the other, which has definite form and consists of organisms or fragments of organisms. Most structureless organic matter is isotropic (there are two anisotropic varieties) and makes up the greater part of the total organic material.

21. UWATOKO, K. Genesis of Oil by High Radial Axial Pressure. Bull. Am. Assoc. Petrol. Geol., vol. ly, 1932, pp. 1029-1037.

High radial axial pressure applied to coal and oil shales from Colorado, Calif., and Fushun generated oil without deforming the test piece by fracture or flow. Liquid and solid oil formed because of the effect of high compression, and the amount produced increased with the pressure applied to the test piece. If the plane of sedimentation of the rock was arranged perpendicular to the orientation of the axial pressure, a large amount of oil was generated. By contrast, if the plane of sedimentation of the same rock was placed parallel with the orientation of the axial pressure, the amount of oil generated was small. After compression, the color of the test piece became darker, and polished specimens had a more resinous or greasy surface.

22. USPENSKII, V. A. (Concerning the Organic Material of Diktyonemic Shale.) Khim. Tverdogo Topliva, vol. 9, 1938, pp. 7-17.

The large amount of nitrogen present in organic material of rocks of the lower Paleozoic era (Leningrad region) showed that humic deposits may contain chitin that may rearrange and eventually form humic acids of high nitrogen content. Some shales contain organic material that is completely free of alkali-soluble humic acids. These shales may be a mixture of fatty and humic material with high-sulfate sulfur content that resembles asphaltic rather than humic materials.

23. LUTS, K. (The Estonian Combustible Shale Kukersite - Its Chemistry Technology and Analysis.) Reval Pub. Co., Reval (Tallin) Estonia, 1944, 460 pp.

Nearly all investigators, except Cunningham-Craig, believe that kukersite represents a maritime product of plant origin. In all probability the deposition of the material that formed kukersite took place in large open seas, at a depth of at least 200 meters and in quiet water not subject to the motion of the sea. The temperature at that depth may have been warm; that of the surface was not below 15° C. Variation in the temperature of the water had an effect upon the alternation of the kukersite and the limestone layers in the deposit. Decaying process probably changed the original algal masses to the present kukersite.

24. BARB, CLARK F. The Origin of the Hydrocarbons in the Uinta Basin. Mines Magazine. (Colorado Sch. Mines), vol. 35, 1945, pp. 555-557.

Oil sands, gilsonite, elaterite (wurtzilite), ozocerite, rosinite, liverite, and oil shales of the Uinta basin may have had a hydrocarbon content of common origin. The original source of nearly all the hydrocarbons was the oil shales of Eocene Age that occur chiefly in the Upper Wasatch and the Green River formations. The hydrocarbons were found mostly in rocks of the Tertiary Age.

No accumulation or trace of hydrocarbons (except oil) was found very far from the oil shale. In many places over an area of several hundred square miles, thin seams and veins of heavy oil or solid hydrocarbons were found leading from the oil shale into sandstones or filling fractures and cracks of the shale. At the old Black Dragon gilsonite mine at Dragon (Utah) a three-way contact of oil shale, oil sand, and gilsonite was found. In many instances, thin seams of tar leading from oil shale into oil saturated sands or oolitic beds saturated with oil were observed. Chert nodules found at one location had grown around hydrocarbon nuclei. In some instances, thin seams of oil leading from the oil shales had impregnated the wall rock to a distance of only a fraction of an inch or sometimes a few inches, whereas a more porous sandstone above or below would be thoroughly saturated. The phenomenon seemed to depend on the porosity and permeability of the rock as well as the viscosity of the hydrocarbon.

It appeared that the organic-rich shales of the Green River formation and part of the Wasatch formation held great quantities of oil-forming material. These hydrocarbons escaped partly as resinous oils of the linseed-oil type and as natural mineral oils, then migrated into more porous zones above and below the shales. This was due to natural compaction of the shales and the drying or shrinkage cracks that formed. The remaining material was probably solid or semisolid and had begun to form the so-called kerogen of the present-day oil shale. Kerogen is merely the polymerized residual products of the original oil from which the more fluid materials escaped.

25. DOBRYANSKII, A. F. (Combustible Shales of the U.S.S.R.) All Union Sci. Inst. for Treatment of Shales, Moscow, U.S.S.R., 1947, 182 pp.

Without exception, the geological character of all known oil shales (including sapropelic shales) indicates an aqueous origin for these minerals. The initial organic material of shales has accumulated in every geological period from Cambrian to the present time. Algae, amoeba, rhizopoda, multicellular organisms, and highly organized animals and plants were the forerunners of an intermediate decomposition product referred to as "pelogen."

After deposition, pelogen is transformed into sapropels under the influence of anerobic conditions. The composition of sapropel depends upon the percentage of humic acids, lignins, bitumens, albumin, and similar materials that were present in the pelogen. Wax and solid hydrocarbons do not contribute significantly to the process of conversion. Factors that affect the composition of the sapropel are prevalence of plant or animal matter, age of the sapropel, and depth of burial. The basic reaction involved in the change from pelogen to sapropel consisted of an increase in carbon and hydrogen content and a decrease in oxygen content. During this change, hydroxyl groups were removed in the form of water, carboxyl in the form of carbon dioxide gas, and ethereal oxygen in the form of carbon dioxide and carbon monoxide.

The chemical conversion of sapropels to kerogen is complex and has not been thoroughly investigated, however, it apparently involves biological and catalytic processes. Kerogen appears to be quite uniform in composition, although the mineral contents of oil shales vary from 5 to 75 percent. In humic minerals the hydrogen content for a given content of carbon is low, and in sapropelic minerals it is higher due to the prevalence of fatty material.

26. FELTS, W. M. Natural Formation of Petroleum-Like Hydrocarbons From Oil Shales. Science, vol. 106, 1947, p. 41.

In many localities throughout the Green River formation there are exposures of porous and permeable rocks containing a viscous liquid hydrocarbon that apparently has been produced naturally from the oil shale. (Author's note. - This material is not a true hydrocarbon, as it contains elements other than carbon and hydrogen.)

The porous and permeable beds were comprised of several thin (2- to 14-inch) layers of volcanic ash, which have been altered to crystalline analcite and chalcedonic silica. Some of these beds, which ranged in porosity from 15 to 20 percent and permeability of 7 to 30 millidarcys, were enveloped by beds of rich organic marlstone. The oil shale had a porosity and permeability near zero, but there was permeability along some of the bedding planes, for sodium carbonate effloresence to form a fresh surface in one month.

In some of these beds of altered volcanic ash the kerogen of the oil shale adjacent to the porous analcitic layer has been transformed to a waxy, semifluid hydrocarbon. This hydrocarbon was identical with the heavier, retorted, shale-oil cuts obtained from kerogen and may be an intermediate step in the production of gilsonite by inspissation of the hydrocarbons produced by natural cracking of pyrobitumens. The above occurrences were offered as field evidence for the natural cracking of pyrobitumens into liquid hydrocarbons resembling some types of petroleum.

27. BRADLEY, W. H. Limnology and the Eocene Lakes of the Rocky Mountain Region. Bull. Geol. Soc. America, vol. 59, 1948, pp. 635-648.

Principles of limnology (science of lakes) and their application to the development of the oil-shale-containing lakes of the Green River formation are given. Lakes in temperate climates are not homogenous bodies but tend to change with the seasons. Because of changes in the density of water over a relatively short temperature range, bodies of water tend to become heterogenous and thermally stratified into layers called epilimnion and hypolimnion. The latter rests on the bottom of the lake and becomes deficient in oxygen but with an abundance of carbon dioxide and hydrogen sulfide. The epilimnion layer is rich in oxygen because of currents set up by wind. A change in season may cause a turnover, and the entire body of water becomes homogenous. Some lakes may also become stratified by dissolved salts and are considered to be chemically stratified.

At the end of Upper Cretaceous time, the Rocky Mountain ranges were upfolded and the intermontane basins formed. Inside these basins, streams eroded new mountains and filled the basins with various mineral deposits. A predominance of mineral carbonates is explained by the fact that the streams draining into the lakes crossed upturned limestones or limy formations. The two factors tending to precipitate the calcium and magnesium carbonates within the lake were: (1) The summer warming of the water, which decreased the solubility of the carbonates, and (2) the photosynthesis of the algae, which removed carbon dioxide and increased the pH of the water. This caused an increase in the carbonate concentration until the solubility product of the carbonates was exceeded and precipitation resulted.

Vast quantities of organic material were deposited in this formation by various methods in amounts from trace to more than 80 percent by volume. The organic material was preserved under stagnant conditions at the bottom of the lake, where oxygen was scarce or absent and hydrogen sulfide was abundant. The presence of saline minerals indicates that a deposit was chemically stratified and the organic material accumulated in a saline hypolimnion. Some oil shales were formed as a result of thermal rather than chemical stratification. A stratified condition existed during most of the period of oil-shale formation and preserved the organic material from complete oxidation.

28. BROOKS, BENJAMIN T. Evidence of Catalytic Action in Petroleum Formation. Ind. Eng. Chem., vol. 44, 1952, pp. 2570-2577.

The problem of determining the genesis of petroleum is essentially chemical in nature. An explanation must be given for the formation of large numbers of paraffins, cycloparaffins, and aromatics from the original organic material at the temperatures known to exist throughout geologic history. There is evidence that the principal source material was unsaturated fatty oils plus an intermediate heavy bitumen that contained no light oils. These materials were changed slowly into typical petroleum by carbonium-ion reactions catalyzed by acid silicates. Heavy oils may be accounted for by the noncatalytic character of the reservoir rock. The organic matter in Colorado oil shale is associated with sodium sesquicarbonate, which may have prevented acid silicate catalysis and conversion to petroleum.

29. HUNT, JOHN M., STEWART, FRANCIS, AND DICKEY, PARKE A. Origin of Hydrocarbons of Uinta Basin, Utah. Bull. Am. Assoc. Petrol. Geol., vol. 38, 1954, pp. 1671-1698.

The hydrocarbons of the Uinta basin occur primarily as veins in oil shale, as saturated sands in contact with oil shale, and as fractures and fissures extending from oil shale. Bituminous lakebeds were the source of the vein hydrocarbons, since these lakebeds still contain appreciable quantities of organic matter with a composition comparable to that of the vein hydrocarbon. The different hydrocarbons of the Uinta basin originated at different geologic times, and the order of their origin was: ozocerite, albertite, gilsonite, and wurtzilite. Changes in the types of hydrocarbons of the Eocene section coincide with changes in the minerals and fossils. Apparently all were controlled by the environment under which the lakebeds were deposited.

Miscellaneous

30. BOTKIN, C. W. Composition of Oil Shale and Shale Oil. Colorado Sch. Mines Quart., vol. 4, No. 4, 1919, pp. 16-17.

31. BRADLEY, W. H. A Contribution to the Origin of the Green River Formation and Its Oil Shale. Bull. Am. Assoc. Petrol. Geol., vol. 9, 1925, pp. 247-262.

32. DAVIS, C. A. Some Fossil Algae from the Oil-Yielding Shales of the Green River Formation of Colorado and Utah. Bull. Geol. Soc. America, vol. 27, 1916, pp. 159-160.

33. ENGLER, C. Formation of the Chief Constituents of Petroleum. Petroleum, vol. 7, 1912, pp. 399-403.

34. HAWLEY, J. E. Generation of Oil in Rocks by Shearing Pressures. III. Bull. Am. Assoc. Petrol. Geol., vol. 14, 1930, pp. 451-481.

35. HUNT, J. M., AND JAMIESON, G. W. Oil and Organic Matter in Source Rocks of Petroleum. Bull. Am. Assoc. Petrol. Geol., vol. 40, 1956, pp. 477-488.

36. RAND, W. P. Generation of Oil in Rocks by Shearing Pressures. IV-V. Further Studies of Effects of Heat on Oil Shales. Bull. Am. Assoc. Petrol. Geol., vol. 17, 1933, pp. 1229-1250.

37. RICH, JOHN LYONS. Probable Fondo Origin of Marcellus-Ohio-New Albany-Chattanooga Bituminous Shales. Bull. Am. Assoc. Petrol. Geol., vol. 35, 1951, pp. 2017-2040.

38. SCHRAMM, E. F. Notes on Oil Shales of Southwestern Wyoming. Bull. Am. Assoc. Petrol. Geol., vol. 4, 1920, pp. 195-208.

39. SEARS, J. D., AND BRADLEY, W. H. Relations of the Wasatch and Green River Formations in Northwestern Colorado and Southern Wyoming, With Notes on Oil Shale in the Green River Formation. Geol. Survey Prof. Papers 132(f), 1924, pp. 93-107.

40. SWAIN, F. M. Stratigraphy of Lake Deposits in Central and Northern Minnesota. Bull. Am. Assoc. Petrol. Geol., vol. 40, 1956, pp. 600-653.

41. TAYLOR, E. McKENZIE. An Examination of Shales Associated with Oil-Bearing Strata in the United States. Jour. Inst. Petrol. Technol., vol. 16, 1930, pp. 681-683.

42. THIESSEN, REINHARDT. Origin and Composition of Certain Oil Shales. Econ. Geol., vol. 16, 1921, pp. 289-300.

43. TWENHOFEL, W. H. Environments of Origin of Black Shales. Bull. Am. Assoc. Petrol. Geol., vol. 23, 1939, pp. 1178-1198.

44. VAN TUYL, F. M., AND PARKER, B. H. The Problem of Petroleum Genesis. Mines Magazine. (Colorado Sch. Mines), vol. 25, 1935, pp. 17-22.

45. WINCHESTER, D. E. Oil Shale in Northwestern Colorado and Adjacent Areas. Geol. Survey Bull. 641(f), 1916, pp. 139-198.

46. _____. Oil Shales of the United States. Econ. Geol., vol. 12, 1917, pp. 505-518.

47. ZO BELL, C. E. Bacterial Release of Oil From Oil-Bearing Materials. World Oil, vol. 126, No. 13, 1947, pp. 36, 39-40, 42, 44, 47; vol. 127, No. 1, 1947, pp. 35-38, 40, 41.

PROPERTIES OF COLORADO OIL-SHALE KEROGEN

Petrographic Characteristics[7]

48. LINKER, SOPHIE. The Relation of Peat to Oil Shale. Chem. Age, vol. 32, 1924, pp. 63-64.

Samples of oil shale from the Green River formation and from Elko (Nev.), Brazil, Austria, and South Africa were examined, and several varieties of shale were found. Green River oil shale represents three of the more common types plus one less common type. These were: contorted shale with a velvety appearance, thin paper shale resembling the curled-up leaves of a book, massive black shale resembling a piece of rubber, and a less common type, which showed the bedding planes very clearly. The Elko (Nev.) shale was a light buff color; the shale from Brazil resembled a piece of petrified peat. When the shales were cut very thin, their colors ranged from yellow to reddish-brown. The composition, as seen under the microscope, was of well-preserved plant material such as spores, pollen grains, fragments of cell tissues, algae, fungi, bacteria, macerated organic residue, small pieces of resin, animal fossils, and translucent bodies.

Oil shale was produced from organic material that accumulated in peat bogs, marshes, or swamps in fresh or salt waters. The organic matter was decomposed by bacterial action. Certain parts of the plants decayed more readily than others. Before lithification occurred, a chemical action took place that changed the softer tissues of the plant debris into a gel. This collodial matter penetrated and surrounded the more resistant fragments and preserved them from further decay. Certain bog waters contain a high percentage of humic acids in solution or collodial suspension and produce insoluble humates when neutralized. These humates are probably the so-called kerogen bodies.

49. CUNNINGHAM-CRAIG, E. H. The Origin and Constitution of Oil Shale With a Practical Application. Proc. World Eng. Cong., Tokyo, 1929, pp. 1-25.

Oil Shales may be dead black (Scotland, Colorado), dark brown (Scotland, New Brunswick, Colorado, Argentina, Bulgaria), gray (Scotland, Colorado), pale yellow (Brazil), pale brick red, olive green, or dark red (Estonia). They might be expected to have a shaly fracture, but this is rare. After having been retorted, a fine laminated or fissile structure is often found. Some oil shales, like the paper shales of New Brunswick, split almost like mica, but most oil shales appear very solid and homogeneous. A good Scottish shale cuts like hard leather or wood, but many of the world's richest shales crumble or break when tried with a knife. Characteristics common to all oil shales are low specific gravity and inorganic matter containing clay. Sandy bands or laminae may be seen in some shales, but the bulk of the material is of a clay nature. Also, intimately mixed with the body of an oil shale is material of organic origin from which oil may be obtained by the action of heat.

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[7] Additional information is presented in items 1, 53, and 61.

The origin of oil shale was due to an adsorption phenomenon involving the combination of more or less inspissated petroleum with colloidal matter.

50. GUTHRIE, BOYD. Isolation and Analysis of Oil-Shale Kerogen. Ch. 8 in Studies of Certain Properties of Oil Shale and Shale Oil. Bureau of Mines Bull. 415, 1938, pp. 107-108.

Samples of oil shale from DeBeque (Colo.) were examined by J. W. Horne and W. W. Purdy. Kerogen viewed under the microscope appeared as a variegated brownish mass, and it was difficult to distinguish individual particles. In thin sections the kerogen varied in color from straw to a reddish-orange to brown. The kerogen particle may be classified into two kinds; one type has a definite physical form and another type is a structureless mass, which composed the major portion of the organic matter.

Composition[8]

51. HARDING, E. P., AND THORDARSON, WILLIAM. Distribution of Sulfur in Oil Shale. Ind. Eng. Chem., vol. 18, 1926, pp. 731-733.

Sulfur was present in Green River oil shale in the form of sulfide, sulfate, and organic sulfur. The resinic sulfur found in the shale oil ranged from one-fourth to all of the organic sulfur.

52. HARDING, E. P. Distribution of Sulfur in Oil Shale. III. Ind. Eng. Chem., vol. 21, 1929, p. 818.

Total sulfur in Green River oil shale from Utah consisted of 37.24 percent sulfide sulfur, 13.26 percent sulfate sulfur, and 49.50 percent organic sulfur. Sulfur in oil shale from Mount Logan (Colo.) was distributed as 46.43 percent sulfide sulfur, 6.30 percent sulfate sulfur, and 47.27 percent organic sulfur.

53. STANFIELD, K. E., FROST, I. C., McAULEY, W. S., AND SMITH, H. N. Properties of Colorado Oil Shale. Bureau of Mines Rept. of Investigations 4825, 1951, 27 pp.

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[8] Additional information is presented in items 6, 19, 50, 56, 109, 120 and 121.

The principal constituents of selected oil-shale samples from the Green River formation at Rifle (Colo.) were calcite, dolomite, illite, and yellow organic material. Other constituents were quartz, feldspar and plagioclase feldspar, pyrite, marcasite, analcite, opal, black opaque organic material, and small woody fragments. Illite was present as minute brown and reddish-brown flakes; quartz, feldspar and plagioclase occurred as angular fragments, which were sorted, distributed, sized, and orientated at random. Granular pyrite and marcasite were scattered throughout the oil shales, and occasionally were concentrated in thin bands paralleling the bedding laminae. Anacite was present as small grains, thin bands, and small lenses. Yellow structureless organic material was intimately mixed with inorganic material and also occurred in long, thin bands or stringers, parallel to the bedding laminae. Brown or brownish-black organic material occurred in thin stringers and as irregular granular masses. This material increased in proportion to the richness of the shale. Occasionally small, black, woody fragments were scattered at random throughout the sections. Microfossils and macrofossils were present, particularly in the leaner shales. Nahcolite (natural sodium bicarbonate) has been found in concretions up to 5 feet across and in layers up to 4 inches thick in oil shales of the Mahogany ledge.

Specific gravities, bulk densities, and heating values of raw shale were related to the oil yields of the shales; consequently, these properties may be used to estimate oil yields of shale samples from the same area. The specific heats of the samples increased slightly as the oil yield increased.

Properties of the assay oils varied slightly for different grades of shale, and gas yields were proportional to the richness of the shale. The assay gases consisted of hydrogen, nitrogen, carbon monoxide, and hydrocarbons, which were derived from the organic material, plus carbon dioxide and hydrogen sulfide derived from both organic and mineral matter. The ash constituents of the spent shale were principally oxides of silicon, calcium, aluminum, and magnesium with smaller amounts of the oxides of iron, sulfur, sodium, and potassium. The amount of oil obtained by retorting was almost proportional to the kerogen content.

The tendency of the shale samples to form a carbonized mass, called oil-shale coke, during retorting did not seem to bear a direct relationship to the quantity of oil produced. However, rich oil shales were more likely to form troublesome cokes.

Six oil-shale samples, crushed to minus 1/2-inch size, were exposed to natural weathering for a period of 5 years. After exposure, the samples yielded an average of 11.4 percent (5.4 gal./ton) less oil and 87.8 percent (2.4 gal./ton) more water than the original samples. None of the samples showed a significant reduction in oil yield by weathering for periods up to 6 months.

The percentage of nitrogen in the oil shale was proportional to the richness and appeared to be derived entirely from the organic material. By contrast, sulfur was not related to the richness of the shale and was present in both the organic and inorganic portions. Pyrite sulfur represented approximately 72 percent of the total sulfur compared with 2 percent sulfate and 26 percent organic sulfur.

The elemental composition of the organic material did not vary greatly for different grades of shale; its average composition corresponded to an empirical formula of $C_6H_{9.86}O_{0.56}N_{0.18}S_{0.04}$. The percentage of benzene-soluble material of 16 samples of various oil yields ranged from 0.7 to 3.2 and tended to increase as the kerogen content of the oil shales increased.

Method of Concentrating Kerogen

54. GUTHRIE, BOYD. Isolation and Analysis of Oil-Shale Kerogen. Ch. 8 in Studies of Certain Properties of Oil Shale and Shale Oil. Bureau of Mines Bull. 415, 1938, pp. 105-123.

Several mechanical procedures were used by J. W. Horne and W. W. Purdy to isolate kerogen from the mineral matter in oil shale from DeBeque (Colo.). Only one method was partly successful. It consisted of using a very small amount of frothing oil in a laboratory machine after the shale was first moistened with alcohol. By this method a large portion of clay and some of the sulfides were eliminated; however, the process did not yield a perfectly clean organic product. Attempts were made to remove organic material by solvent extraction. Ethyl alcohol, methyl alcohol, ethyl ether, chloroform, carbon disulfide, carbon tetrachloride, benzene, petroleum gasoline, and turpentine all extracted from trace to 5 percent of the kerogen. Pyridine extracted 15 to 20 percent, and a maximum of 30 percent kerogen was removed by repeated extractions with pyridine. After the solvent was evaporated, a product was obtained that apparently was altered chemically. Inorganic material was removed from the organic by treatment with concentrated hydrochloric and hydrofluoric acids. The ash content was reduced to 1.3 percent and consisted mainly of magnesium and calcium fluorides, iron and aluminum oxides, and some silicates. Although no positive proof was found to show that the kerogen had not undergone chemical change, neither could it be proved that the material had been affected. The sample contained 78.40 percent carbon, 10.42 percent hydrogen, 1.20 percent sulfur, 2.58 percent nitrogen, 1.03 percent ash, and 6.37 percent oxygen by difference.

55. HUBBARD, ARNOLD B., SMITH, H. N., HEADY, H. H., AND ROBINSON, W. E. Method of Concentrating Kerogen in Colorado Oil Shale by Treatment With Acetic Acid and Gravity Separation. Bureau of Mines Rept. of Investigations 4872, 1952, 8 pp.

The insoluble organic material in a rich oil shale from Rifle (Colo.) was concentrated without any apparent alteration of its original chemical form. Finely pulverized shale was treated with dilute acetic acid at room temperature to remove carbonates. The acid-treated residue was then centrifuged in different liquid mediums ranging from 1.4 to 1.15 gravity to effect a mechanical separation.

By this method it was possible to produce concentrates with ash contents as low as 8.7 percent, largely Fe_2O_3 from pyrite, from an oil shale having an ash content of 48.0 percent. However, the yield of this low ash material constituted only 1 percent of the original shale sample. The kerogen was not significantly altered because the color of the kerogen was not changed, the carbon-hydrogen ratios of all fractions were similar, and the oil-kerogen and water-kerogen ratios calculated from assay data showed little variation.

Straight-line relationships were obtained when the elemental composition of the sink or float samples were plotted against their ash content. By extrapolating to zero percent ash, it was possible to estimate the following ultimate composition of ash-free kerogen: 78.0 percent carbon, 10.3 percent hydrogen, 2.6 percent nitrogen, 1.2 percent sulfur, and 7.9 percent oxygen by difference.

56. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1955. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 5237, 1956, pp. 64-65.

Oil shale from Rifle (Colo.), having an ash content of 54.7 percent and assaying 57.1 gallons of oil per ton, was leached with dilute acetic acid to remove mineral carbonates. A paste, made by mixing this material with oil, was ground for approximately 1,000 hours in the presence of water. During the grinding period the aqueous suspensions were discarded periodically. The final organic concentrate contained 17.2 percent ash, of which 7.0 percent was ash derived from the mullite grinding equipment. Separation of the shale components was attempted by the use of sonic energy, mechanical shaking and ultracentrifugation. None of these methods caused significant concentration of the shale constituents.

Studies were also made on the ultimate composition of the organic material in oil-shale concentrates. The inorganic ash was determined by ignition at 1,000° C. A correction for the effect of ashing the mineral matter was made by determining the difference between the loss due to volatilization of pyrite sulfur and gain in weight due to oxidation of pyrite iron to Fe_2O_3 and Cu_2O to CuO.

The following results were obtained for three organic concentrates: (1) Oil shale leached with acetic acid--77.25 percent carbon, 9.85 percent hydrogen, 2.62 percent nitrogen, 1.16 percent sulfur, and 9.12 percent oxygen; (2) oil shale leached with HCl and HF acids--77.66 percent carbon, 9.58 percent hydrogen, 2.58 percent nitrogen, 0.67 percent sulfur, and 9.51 percent oxygen; and (3) oil shale leached with acetic acid followed by oil grinding--76.22 percent carbon, 9.82 percent hydrogen, 2.53 percent nitrogen, 0.80 percent sulfur, and 10.63 percent oxygen.

Reaction by Heat[9]

57. GAVIN, MARTIN J., AND SHARP, LESLIE H. Short Papers From the Cooperative Oil-Shale Laboratory. Colorado Cooperative Oil-Shale Investigation Bull. 1, 1921, 68 pp.

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[9] Additional information is presented in items 53, 64, 68, 78, 114, 120, 121, and 171.

During the retorting of Colorado oil shale, gas evolution began at temperatures between 200° and 250° F. and yielded an average of about 1,770 cubic feet per ton. Water formed at about the same temperature and was evolved throughout the oil-production stage. The latter stage occurred at 625° to 1,150° F., but 96 percent of the oil was formed at temperatures up to 900° F. Maximum yields of oil resulted from slower rates of retorting.

58. GEORGE, R. D. Oil Shales of Colorado. Colorado Geol. Survey Bull. 25, 1921, 78 pp.; Railroad Redbook, vol. 38, 1921, pp. 793-796, 865-868, 929-933.

Laboratory studies were made on the retorting, the refining and fractionation of retort products, and the composition of the distillate fractions obtained from Colorado oil shale. Analytical results are given. Very little of the retorted oil is present in the shale as true hydrocarbons.

59. McKEE, RALPH H., AND LYDER, E. E. The Thermal Decomposition of Shales. I. Heat Effects. Ind. Eng. Chem., vol. 13, 1921, pp. 613-618.

Sixty-mesh oil shale from Grand Valley (Colo.) was heated in a sealed container for 1 to 8 hours at temperatures of 374° to 425° C., and the amount of kerogen made soluble was determined. The pyrobitumens did not decompose to primary distillation products (oil), as the first substance obtained was a heavy solid or semisolid bitumen. This bitumen was formed at a definite temperature between 400° and 410° C. in the instance of this particular shale. The petroleum oils formed from the shale resulted from decomposition or cracking of the heavy bitumen.

60. _____. The Thermal Decomposition of Oil Shales. II. Determination of the Heat of Reaction in Their Thermal Decomposition. Ind. Eng. Chem., vol. 13, 1921, pp. 678-684.

The purpose of this research was to study the heat involved and the primary effect of heat on oil shale from Grand Valley (Colo.). The heat of reaction for decomposing the oil shale to gas and oil ranged from 421 to 484 calories per gram of oil and gas produced. The coefficient of conductivity was 0.00086 gram calories per cubic centimeter per second.

61. McKEE, RALPH H., AND GOODWIN, RALPH T. A Chemical Examination of the Organic Matter in Oil Shales. Colorado Sch. Mines Quart., vol. 18, No. 1, supp. A, 1923, 41 pp.; Ind. Eng. Chem., vol. 15, 1923, pp. 343-349.

Samples of oil shale from DeBeque (Colo.) were examined by a microscope at a magnification of 50 diameters. Thin sections showed clear quartz grains, dense black grains of pyrite coalesced to form irregular masses, mixed clay substances, sericitic products, and carbonates. The brown and reddish bituminous matter stained much of the rock, but it was usually broken into laminae by gray streaks and bands. Occasionally, very dark streaks were associated with black or dark-brown specks of bituminous matter.

Oil shales were treated with sulfur dioxide, selenium oxychloride, sulfuryl chloride, and chlorine gas. After 24 hours of treatment with sulfur dioxide, an extract of 0.3 percent was obtained from Colorado oil shale. The small amount of extract was a dark brown to black resinlike semisolid. The low yield of extract indicated that the kerogen of oil shale is not an unsaturated type of organic material that is attacked by liquid sulfur dioxide. Samples of Colorado oil shale gave an average increase in weight of 20.9 percent when treated with selenium oxychloride, and both the shale residue and extract contained red selenium. A sample of Colorado oil shale increased 9.3 percent in weight after refluxing 12 hours with sulfuryl chloride. California shale increased in solubility in alcohol from 1.5 percent to 47.7 percent by chlorination with sulfuryl chloride. Colorado oil shale was suspended in carbon tetrachloride, and chlorine gas was bubbled through the liquid for 36 hours. The shale increased 0.6 percent in weight and contained 6.2 percent alcohol-soluble material, compared with 1.4 percent before chlorination.

Oven-dried oil shale from DeBeque (Colo.) of 40- to 60-mesh per inch size was extracted with various solvents in a Sohxlet-type apparatus. Percentage yields of extracts by the various solvents were aniline, 1.8; absolute alcohol, 1.43; acetone, 1.48; petroleum ether, 1.39; m-cresol, 0.87; pyridine, 2.04; phenol, 0.87; carbon disulfide, 1.00; carbon tetrachloride, 2.04; benzene, 2.23; and chloroform, 2.41 percent.

Only part of the kerogen of the shale could be extracted by solvents, and the material extracted did not appear to be an oil and only resembled oil when subjected to destructive distillation. This indicated that the shale contained no oil as such but contained an organic material from which oil may be produced by destructive distillation.

Samples of raw oil shale and pyrolyzed shale from Grand Valley (Colo.) were heated side by side under the same conditions. The extent to which the temperature of the raw shale became higher or lower than the "spent" shale in the various pyrolytic stages was determined. In another experiment 40-mesh oil shale was retorted under 8 mm. of Hg pressure. The distillates were analyzed and then distilled at atmospheric pressure.

The oil shale showed an endothermic reaction from 350° to about 400° C., followed by an exothermic change from 395° to 420° C. Except for small variations, the reaction was still exothermic up to about 500°, and it became markedly exothermic above this temperature. These results indicated that the organic content of the shale consists of a mixture of substances. Redistillation of the intermediate product obtained by vacuum retorting of oil shale increased the content of saturates 27 percent. This indicated that the final pyrolysis products were not liberated as such from the shale kerogen. Therefore, the decomposition of kerogen to form oil appeared to occur in two stages. A primary decomposition took place in which the insoluble kerogen was changed into a soluble solid or semisolid (this process may be deploymerization). This "intermediate product" had a composition different from that of kerogen, as indicated by analyses and the increased solubility of the product. It was unstable, and a second decomposition changed it into lighter oils of greater stability and higher saturation. When the intermediate product was only slightly decomposed, the oil was less saturated, unstable, and heavier. Both the primary and the secondary decompositions were accompanied by a series of thermal reactions. The formation of oil from shale was as follows: Kerogen → intermediate product → shale oil.

62. MAIER, CHARLES G., AND ZIMMERLY, STUART R. The Chemical Dynamics of the Transformation of the Organic Matter to Bitumen in Oil Shale. Utah Univ. Res. Investigation Bull., vol. 14, 1924, pp. 62-81.

Experimental data showed the relationship between the amount of bitumen formed from oil shale from Soldiers Summit (Utah) and the temperature and period of pyrolysis. Samples of shale were heated in a constant temperature bath for definite periods, and the amount of bitumen formed was determined by extraction.

Bitumen formation was a function of the temperature and time of heating. This point may have been missed by other observers, as the rate was slow at low temperatures, and the bitumen decomposed as soon as it formed unless precautions were taken. The amount of bitumen formed was independent of temperature; therefore, the ultimate yield of bitumen can be obtained at either low or high temperatures if the heating time is sufficiently long. (Author's note - Recent work does not entirely agree with this statement.) The values obtained for the specific reaction-rate constant $\underline{k}$ for various temperatures may be used to calculate the rate of transformation of the organic matter at conditions impossible to determine experimentally. These data also indicate that the formation of bitumen is an endothermic process.

63. STADNICHENKO, TAISIA, AND WHITE, DAVID. Microthermal Observations of Some Oil Shales and Other Carbonaceous Rocks. Bull. Am. Assoc. Petrol. Geol., vol. 10, 1926, pp. 860-876.

The temperature at which fossil components of bituminous shales, oil shales, and other carbonaceous rocks undergo changes in optical character, volume, and state of matter was determined.

The four principal kinds of organic matter present in oil shale are ulmic binder or groundmass, spores and pollen exines, cuticles and cuticular secretions, and fatty or oily algae. The different organic fossil constituents in a given section of oil shale have different temperature zones of change (color and volume). In certain fossil constituents the main volatilization occurs instantaneously at definite temperatures; in others the changes may not be so clearly defined. The ulmic groundmass (also referred to as humic groundmass or biochemical concentrate) regarded by many as the source of oil, seems in most cases to pass through two or more phases or zones of change with reduction in volume at different temperatures. In its late stage of carbonization, the ulmic groundmass appears to be comparable to coal in the later stage of coking. Heavy high-boiling hydrocarbons deficient in hydrogen were driven off at higher temperature. Oxidation reduced the yield of oily and volatile substances. In some rocks the temperature at which changes occurred was higher when the section was heated rapidly, but where melting and volatilization took place at a definite temperature, time and rate of heating seemed to have little or no effect. In the final stage of carbonization the thin section contained a black carbon residue.

64. McKEE, RALPH H., AND MANNING, PAUL D. V. Shale Oil. II. Gases From Oil Shale. Oil Bull., vol. 13, 1927, pp. 489-493, 729-737, 837-843.

Oil shale (Author's note - presumably from Colorado) was pyrolyzed, and the gaseous products obtained were studied. The organic material present in oil shale contains carboxyl groups that lose carbon dioxide during pyrolysis before the formation of soluble bitumen. Nitrogen was evolved as ammonia in two stages and was not continuous. The first evolution was from loosely combined nitrogen structures, whereas the second was from more stable forms. No hydrocarbons were present as such in the kerogen.

The gaseous products from oil-shale pyrolysis were similar to those obtained by distillation of colophony, amber, coal, and wood. This places the kerogen of the oil shale in the same series of carbonaceous substances as those from which coals are formed. Kerogen appeared to be decomposed in three steps; namely, to insoluble bitumen, to soluble bitumen, and to oil (gas evolution accompanied each step). Its low solubility and the character of its pyrolytic gas indicated that kerogen is largely a resinous residue from vegetation of the past era and may have been formed by the transportation of coal-forming organic debris to inland salty lakes or carried to the sea by clay-laden waters. The salt water and the natural settling action precipitated the clay and organic matter in an almost homogeneous deposit. Oil shales have existed to the present time because they have not been subjected to high pressures or elevated temperatures that would have changed them to petroleum.

65. GUTHRIE, BOYD. Nitrogen and Its Compounds in Oil Shale and Shale Oil. Ch. 9 in Studies of Certain Properties of Oil Shale and Shale Oil. Bureau of Mines Bull. 415, 1938, pp. 134-135.

At a temperature of about 325° C., kerogen from DeBeque (Colo.) softens, swells, and becomes black and has the general appearance of a soft bitumen. After heating to 325° C. the solid nitrogen compounds in oil shale were converted into materials that were soluble in organic solvents such as carbon disulfide, benzene-alcohol mixtures, carbon tetrachloride, and trichloroethylene. This was followed by a physical and pyrolytic change, which might be termed the water-producing period and occurs between 300° and 405° C. Apparently at these temperatures, the water of combination from the inorganic and organic constituents was released. Simultaneously, ammonia, easily volatilized organic nitrogen compounds, and hydrogen sulfide were formed. After the water was liberated, these other gases were produced throughout the remainder of the retorting period. As the temperature increased, the pyrolysis continued into another stage, and at approximately 390° C. heavy oil vapors and gas began to be formed and distilled from the mass. This action continued as the temperature increased, up to 500° or 600° C., where the production of condensable oil vapors ceased. Noncondensable hydrocarbons and ammonia continued to be produced, leaving a carbonized or completely spent shale.

66. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior, 1946, p. 51.

Two-inch cubes of oil shale from Rifle (Colo.) were subjected to dielectric heating by an electric current with a frequency of 10 to 30 megacycles. The maximum temperature reached in the cubes was 380° F. (193° C.) for 130 seconds of heating. Several factors were encountered that made the heating difficult, as splitting of the blocks, evolution of vapors, and burning of the shale. No other changes indicating alteration of kerogen were observed. The shale showed a dielectric constant of 4.7 for a sample cut parallel to the bedding planes of the shale and 6.7 for a sample cut perpendicular to the bedding planes.

67. _____. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1948. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 4457, 1949, pp. 38-39.

Oil shale from Rifle (Colo.) contains a solid organic material that is converted to oil, gas, and fixed carbon upon heating. It should be possible to control this conversion so as to produce more volatile fuels rather than the heavy residual type of fuel customarily produced; however, this has never been accomplished successfully. If the sulfur, nitrogen, and oxygen present in kerogen could be eliminated without loss of carbon and hydrogen, 40 to 60 percent more oil could be produced. The organic material apparently dehydrogenates and dealkylates, forming high yields of gas and coke.

Cracking of shale-oil fractions may be considered as a race between rupture of partly hydrogenated rings with the formation of gasoline-boiling-range material and dehydrogenation and dealkylation of these same structures with the formation of high yields of gas, coke, and very little low-boiling distillates. This is not the complete mechanism. While the kerogen in oil shale contains enough hydrogen to form a much better quality of oil than usually is obtained, kerogen is still hydrogen-deficient compared with most petroleums, and kerogen lies between coal and petroleum in hydrogen content. Coals, except anthracites, contain 5 to 6 percent hydrogen; most petroleums contain 11 to 15 percent hydrogen, and kerogen contains 8 to 11 percent hydrogen. Shale oil, as usually produced, is in the poorer grades of petroleum and contains 11 to 12 percent hydrogen.

68. HUBBARD, ARNOLD B., AND ROBINSON, W. E. A Thermal Decomposition Study of Colorado Oil Shale. Bureau of Mines Rept. of Investigations 4744, 1950, 24 pp.

A thermal decomposition study of the kerogen in three grades of oil shale from Rifle (Colo.) was made at different temperatures by heating the shales in the absence of oxygen at atmospheric pressure and measuring the decomposition products (gas, oil, and bitumen) formed. From these data the specific reaction rate $\underline{k}$ for the thermal decomposition of kerogen was determined for each temperature studied. Using these data, it was possible to calculate the time required to accomplish a given amount of decomposition within the temperature range studied.

The relation of temperature to decomposition rate was comparable for each of the three grades of shale samples whose oil yields ranged from 26.7 to 75.0 gallons of oil per ton of shale. The formation of gas and oil continued throughout the heating period, but the formation of bitumen increased to a maximum and then dropped to zero as the heating continued. This indicated that the kerogen was converted to bitumen, which, upon subsequent heating, was cracked into gas, oil, and organic residue. A straight-line relationship was obtained for the thermal decomposition of kerogen at temperatures of 350° to 437° C. A break in the curve occurred at 437° C. above which another curve having a different slope was obtained. This may have been due to difficulty in measuring the rapid decomposition of kerogen above 347° C. and the time lag in heating the sample to the desired temperature. The reaction rate below 437° C. is expressed by the equation:

$$\log k \times 10^2 = -13{,}572\ 1/T\ (^\circ\text{Kelvin}) + 20.45$$

while the reaction rate above 437° C. is expressed by the equation:

$$\log k \times 10^2 = -5{,}549\ 1/T\ (^\circ\text{Kelvin}) + 9.14$$

By these equations, the value of k can be calculated for any temperature between 350° and 525° C.

69. ROBINSON, W. E., AND HUBBARD, ARNOLD B. Study of Preheating Colorado Oil Shale. Bureau of Mines Rept. of Investigations 4787, 1951, 13 pp.

A laboratory study was made to determine if drying and preheating oil shale from Rifle (Colo.) with waste retort gases had an appreciable effect on the oil yield. Samples of crushed oil shale were heated at subretorting temperatures (175° to 350° C.) in a specially constructed electric furnace by gases similar in composition to waste gases from oil-shale retorts.

Preheating oil shale with nitrogen or a reducing mixture had no effect upon the oil or water yield. Oxygen in the preheating gas caused a decrease of oil and an increase in water. Generally the oil yield decreased with (a) increase in oxygen content, (b) increase in temperature, (c) increase in heating time, and (d) decrease in the particle size of the shale. The decrease in oil and the increase in water resulting from preheating were due to oxidation of the benzene-insoluble organic material (kerogen) rather than to oxidation of the benzene-soluble organic material (natural bitumen) in the shale. Water, but no CO_2, was formed when shale was heated at 175° C. in the presence of oxygen, and water, plus CO_2 (oxidation products), was formed when shale was heated at 200° C. in the presence of oxygen. These observations suggested the possibility of two types of oxidation when the shale was heated under the different conditions of this study. The formation of these oxidation products indicated dehydrogenation when the oil shale was heated at 175° C., and slow combustion when the shale was heated at 200° C. There was no appreciable conversion of kerogen to soluble products below 325° C.

70. HEADY, HOWARD H. Differential Thermal Study of Colorado Oil Shale. Am. Mineral., vol. 34, 1952, pp. 804-811.

Original from THE OHIO STATE UNIVERSITY

The purpose of this study was to determine whether any mineral constituents, especially clays, could be identified in oil shale from Rifle (Colo.) and to determine the types of thermal reactions taking place during pyrolysis of the organic constituents of the shale.

An endothermic dip occurred at 450° to 475° C., where kerogen was converted to gas, oil, and organic residue; but it was not determined whether the conversion reaction was endothermic in character or whether heat was absorbed in the vaporization of the conversion products. The decomposition of the organic matter affected the oil-shale clays in such a way that the magnitude of their characteristic thermal peaks was decreased; consequently, clays present in oil shale were not identified. Carbonates, calcite, dolomite, and illite clay were present in all the samples studied.

71. JENSEN, H. B., BARNET, W. I., AND MURPHY, W. I. R. Thermal Solution and Hydrogenation of Green River Oil Shale. Bureau of Mines Bull. 533, 1953, 42 pp.

Crushed oil shale from Rifle (Colo.) was treated in a small autoclave at temperatures of 700° to 950° F. (371° to 510° C.). The effect of temperature, reaction time, type of solvent, and richness of the oil shale upon conversion of organic material to soluble products was determined. Samples of shale were subjected to hydrogen pressures from 300 to 4,300 p.s.i.g. for various periods at the above temperatures.

Highest yields of gas and oil obtained without using hydrogen pressure were equivalent to 119 percent of the product yield by Fischer assay. With a high partial pressure of hydrogen, yields equivalent to 126 percent of Fischer assay were obtained. Nondistillable oil, equivalent to approximately 100 percent of the organic matter in the oil shale, was obtained without hydrogen pressure. With hydrogen pressure, the yield of nondistillable oil was 60 to 70 percent of the organic matter present in the oil shale. Part of this heavy nondistillable oil was formed by polymerization and condensation of the shale-oil solvent used. These reactions, as well as cracking of the solvent to form gas and a carbonaceous deposit on the shale, are unfavorable features of the process.

72. DI RICCO, LEO, AND BARRICK, PAUL L. Pyrolysis of Oil Shale. Ind. Eng. Chem., vol. 48, 1956, pp. 1316-1319.

Oil shale from Rifle (Colo.) was pyrolyzed and the decomposition rates were determined over the temperature range of 250° to 465° C. and pressures of 625 to 50 mm. of mercury. The sample was rapidly heated and cooled so that the heating times could be accurately measured. Temperature and pressure were accurately controlled, and provisions were made for the recovery of retorted material (oil and spent charge). An inert gas was used to sweep the oil vapors from the retorting zone to minimize oxidation and cracking.

Kerogen decomposed (250° to 465° C.) in a manner that may be represented by the rate equation for a first-order reaction as:

$$\log_{10} k = \frac{-17,800}{\text{temp. (deg. Rankine)}} + 15.4$$

The effect of pressure between 625 and 50 mm. of mercury on the rate of retorting of oil shale was insignificant over the temperature range studied.

Reaction by Chemicals[10]

73. BROWER, F. M., AND GRAHAM, E. L. Some Chemical Reactions of Colorado Oil-Shale Kerogen. Ind. Eng. Chem., vol. 50, 1958, pp. 1059-1060.

Oil shale from Rifle (Colo.) was treated with chlorine gas, hydrogen bromide, nitric acid-sulfuric acid mixture, fuming sulfuric acid, chlorosulfonic acid, air at temperatures from 200° to 375° C., acetic anhydride in the presence of stannic chloride, and maleic anhydride. Oil shale treated with chlorine contained 21.85 percent chlorine; oil shale treated with bromine contained 13.46 percent bromine. When treated with nitric acid, the shale contained 3.45 percent nitrogen. Oil shale sulfonated with chlorosulfonic acid contained 6.06 percent sulfur and lost 50 percent in weight. (Author's note - Colorado oil-shale kerogen averages 2.6 percent nitrogen, 1.1 percent sulfur, and little or no halogens.) The principal products formed by air oxidation were water, oxides of carbon, and water-insoluble regenerated humic acid. A sample of oil shale treated with acetic anhydride did not give the Friedel-Crafts reaction, and maleic anhydride also failed to react. Colorado oil-shale kerogen contains approximately one double bond for each 16 to 22 carbon atoms. Although kerogen is generally regarded as a nonbenzenoid material it undergoes, to a limited extent, some substitution reactions typical of aromatic compounds.

Physical Properties[11]

74. GAVIN, MARTIN J., AND SHARP, LESLIE H. Physical and Chemical Data on Colorado Oil Shale. Eng. Min. Jour., vol. 110, 1920, pp. 579-580.

The following physical properties of oil shale from DeBeque (Colo.) and its products by retorting were determined: weight per cubic foot (bulk density) 53.775 pounds per cubic foot (p.c.f.) for run-of-mine shale and 58.200 p.c.f. for 1/4-inch raw shale size; apparent specific gravity of raw shale, 1.92 to 2.06; specific heat, 0.265 (means 20° to 90° C.) for raw shale and 0.223 (means 20° to 90° C.) for spent shale; heat of combustion, 2,460 calories per gram (cal./g.) for raw shale and 600 cal./g. for spent shale; and specific gravity of shale oil at 60° F., 0.905.

75. FINLEY, W. L., AND BAUER, A. D. Coking of Oil Shales. Bureau of Mines Tech. Paper 398, 1926, 10 pp.

The coking (fusion or melting point) of Colorado and Elko (Nev.) oil shale did not bear any direct relationship to the yield or quality of oil produced from the shale. A coking shale melted to a plastic or semifluid condition after which it decomposed to form a coke. Oxidation of oil shale by air at a temperature of 125° to 135° C. destroyed the coking property. Removal of the carbon tetrachloride-soluble bitumen did not affect the coking tendency, but extraction with pyridine did remove some of the coking constituents from the shale.

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[10] Additional information is presented in items 61 and 165.
[11] Additional information is presented in items 53, 68, 121 and 171.

76. SHAW, R. J. Specific Heat of Colorado Oil Shales. Bureau of Mines Rept. of Investigations 4151, 1947, 9 pp.

Average specific heats were determined for five samples of oil shale from Rifle (Colo.) assaying 1 to 89.2 gallons of oil per ton and spent shales obtained by retorting two of the samples. The mean specific heats above 77° F. are correlated by the following equations:

$$\text{Raw shale:} \quad S_{os} = 0.172 + (0.067 + 0.00162G)10^{-3}\ T$$

$$\text{Spent shale:} \quad S_{ss} = 0.174 + 0.051 \times 10^{-3}\ T$$

where S_{os} and S_{ss} are mean specific heats between 77° F. and T° Rankine and G is the assay value in gallons of oil per ton of shale.

77. SOHNS, H. W., MITCHELL, L. E., COX, R. J., BARNET, W. I., AND MURPHY, W. I. R. Heat Requirements for Retorting Oil Shale. Ind. Eng. Chem., vol. 43, 1951, pp. 33-36.

The total heat necessary to retort oil shale from Rifle (Colo.) to shale oil and accompanying byproducts under conditions that would exist in commercial practice was determined. The heat of retorting, measured above 77° F. ranged from 104 to 356 British thermal units (B.t.u.) per pound for a 28-gallon-per-ton raw shale and from 261 to 378 B.t.u. per pound for a 57-gallon-per-ton shale. The heat content above 77° F. of the spent shales was determined at temperature intervals from 500° to 1,110° F. and ranged from 94 to 272 B.t.u. per pound.

78. ALLBRIGHT, C. S., VAN METER, R. A., DINNEEN, G. U., AND BALL, J. S. Analyses of Crude Shale Oil. 2. Some Brazilian and U.S.A. Oils. Bureau of Mines Rept. of Investigations 5286, 1956, p. 6.

Based on average results for 1-foot core samples from one test hole through the Federal Bureau of Mines Demonstration mine at Anvil Points (Colo.), the richness of oil shale affected the yields and properties of the assay products. Oils from shales yielding up to 10 gallons of oil per ton had the lowest average pour points of 55° F., but the highest specific gravities of 0.944 at 60°/60° F. and viscosities of 282 Saybolt Universal seconds at 100° F. By contrast, oil from a rich oil shale assaying 50 gallons of oil per ton, had a pour point of 85° F., specific gravity of 0.914 at 60°/60° F., and viscosity of 93 Saybolt Universal seconds at 100° F. However, despite this evidence, data from studies of oil shales from other points in the Colorado formation failed to reveal any particular relation between properties of the Fischer assay oils and shale richness. Therefore, the characteristics of any assay oil cannot always be predicted from a knowledge of the richness of the parent shale.

Miscellaneous

79. ALDERSON, W. C. Colorado Oil Shales. Petrol. Times, vol. 14, 1925, p. 227.

80. ANDERSON, VICTOR C. Oil Shale. Colorado Sch. Mines Quart., vol. 18, No. 1, supp. B, 1923, 28 pp.

81. BALL, JAMES O. Oil Shales of the West. Compressed Air Magazine, vol. 50, 1945, pp. 156-160.

82. BOTKIN, C. W. Composition of Oil Shale and Shale Oil. Colorado Sch. Mines Quart., vol. 14, No. 4, 1919, pp. 16-17.

83. BUREAU OF MINES. Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act, 1945, 44 pp.; 1946, 82 pp.; 1947, 128 pp.

84. _____. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior. Part II. Bureau of Mines Rept. of Investigations (R. I.) 4457, 1949, 56 pp.; R. I. 4652, 1950, 70 pp.; R. I. 4771, 1951, 88 pp.; R. I. 4866, 1952, 86 pp.; R. I. 4943, 1953, 70 pp.; R. I. 5044, 1954, 55 pp.; R. I. 5119, 1955, 115 pp.; R. I. 5237, 1956, 80 pp.

85. ERTL, T. Sodium Bicarbonate (Nahcolite) From Colorado Oil Shale. Am. Mineral., vol. 32, 1947, pp. 117-120.

86. FIELDNER, A. C., AND FISHER, PAUL. Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas. Bureau of Mines Inf. Circ. 7304, 1945, 18 pp.

87. FRANKS, A. J. Colorado Shale Oils. Chem. Met. Eng., vol. 25, 1921, pp. 778-782.

88. FROST, I. C., AND STANFIELD, K. E. Estimating Oil Yield of Oil Shale From Its Specific Gravity. Anal. Chem., vol. 22, 1950, pp. 491-492.

89. GAVIN, M. J. Oil Shale: An Historical, Technical and Economic Study. Bureau of Mines Bull. 210, 1924, pp. 156-179.

90. HORNE, J. W., AND BAUER, A. D. Comparison of Oils Derived From Coal and From Oil Shale. Bureau of Mines Rept. Investigations 2832, 1927, 34 pp.

91. KARRICK, L. C. Some Factors Affecting Products From Destructive Distillation of Oil Shales. Bureau of Mines Rept. Investigations 2324, 1922, 5 pp.

92. LENKER, VICTOR. Some Properties of Selenium Oxychloride. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 29-35.

93. MAIR, C. G., AND DRAPEAU, J. E. Effect of Various Gases on the Recovery of Ammonia From Oil Shale. Univ. of Utah Bull. 14, 1924, pp. 42-61.

94. McKEE, R. H. Shale Oil. Ind. Eng. Chem., vol. 14, 1922, p. 847.

95. PRIEN, C. H. Oil Shale and Shale Oil. Ch. in Oil Shale and Cannel Coal. The Institute of Petroleum, London, vol. 2, 1951, pp. 76-111.

96. _____. Pyrolysis of Coal and Shale. Ind. Eng. Chem., vol. 40, 1948, pp. 1649-1659; vol. 41, 1949, pp. 1906-1914; vol. 42, 1950, pp. 1731-1739; vol. 43, 1951, pp. 2006-2015; vol. 44, 1952, pp. 2064-2072; vol. 45, 1953, pp. 2022-2034; vol. 46, 1954, pp. 1881-1888; vol. 47, 1955, pp. 1911-1915; vol. 48, 1956, pp. 1653-1657; vol. 49, 1957, pp. 1548-1552.

97. SCHRAMM, E. F. Notes on Oil Shales of Southwestern Wyoming. Bull. Am. Assoc. Petrol. Geol., vol. 4, 1920, pp. 195-208.

98. SHULTZ, E. B., GUYER, J. J., AND LINDEN, H. R. Pyrolysis of Crude Shale Oil. Ind. Eng. Chem., vol. 47, 1955, pp. 2479-2482.

99. SMITH, J. W. Specific Gravity-Oil Yield Relationship of Two Colorado Oil-Shale Cores. Ind. Eng. Chem., vol. 48, 1956, pp. 441-444.

100. STANFIELD, K. E., AND THORNE, H. M. Oil Shale Research and Process Development. Ind. Eng. Chem., vol. 43, 1951, pp. 16-20.

101. THORNE, H. M., MURPHY, W. I. R., BALL, J. S., STANFIELD, K. E., AND HORNE, J. W. Characteristics and Utilization of Oil Shale and Shale Oil. Ind. Eng. Chem., vol. 43, 1951, pp. 20-27.

102. THORNE, H. M., MURPHY, W. I. R., STANFIELD, K. E., BALL, J. S., AND HORNE, J. W. Green River Oil Shale and Products. Ch. in Oil Shale and Cannel Coal. The Institute of Petroleum, London, vol. 2, 1951, pp. 301-344.

CONSTITUTION OF COLORADO OIL-SHALE KEROGEN

Soluble Kerogen[12]

103. GAVIN, M. J., AND AYDELOTTE, J. T. Solubility of Oil Shales in Solvents for Petroleum. Bureau of Mines Rept. of Investigations 2312, 1922, 4 pp.

Samples of 20- to 60-mesh-per-inch oil shale from DeBeque (Colo.) were extracted in a Sohxlet-type apparatus with various solvents. The following yields of extracts in weight-percent of raw shale were obtained: Carbon tetrachloride 2.04 percent, carbon disulfide 1.85 percent, acetone 1.33 percent, benzene 2.23 percent, and chloroform 2.41 percent. In all instances the extracts appeared to be different from the oil produced by distillation of the shale. This showed that oil shales contained no oil as such.

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[12] Additional information is presented in items 5, 6, 49, 61, and 120.

104. VAN TUYL, F. M., AND BLACKBURN, C. O. Little Petroleum Formed by True Oil Shale in Nature. Oil Gas Jour., vol. 24, No. 10, 1925, pp. 188-190.

Samples of oil shale from DeBeque (Colo.) were extracted for a total of 311 hours with chloroform, and a total of 18.6 percent of the kerogen was made soluble. This oil or bitumen was derived from a more soluble part of kerogen. Kerogen has previously been regarded as insoluble in organic solvents, but investigations showed that the kerogen of certain oil shales became soluble after long contact with chloroform and that the amount of oil extracted varied directly with the time of treatment.

105. HAWLEY, J. E. Generation of Oil in Rocks by Shearing Pressures. I. The Problems - Methods of Determining the Soluble Organic Content of Oil Shales. Bull. Am. Assoc. Petrol. Geol., vol. 13, 1929, pp. 303-328.

The theory of Cunningham-Craig for the formation of oil shale was questioned. Oxidation of the insoluble kerogen present in Colorado oil shale produced new soluble matter and showed that all the kerogen was not simply adsorbed by the mineral matter. Neutralization of the charges on the adsorbed material should increase the solubility of the adsorbed organic material; however, this did not happen. Formation of soluble fatty acid by the oxidation of kerogen suggested that the soluble material in oil shale may have been formed by oxidation and that oxidation may have been a factor in the formation of kerogen. Oil shale from DeBeque (Colo.) contains two kinds of organic matter; one part (about 2 percent) is readily soluble in common organic solvents and another part is insoluble in organic solvents.

Grinding oil shale at room temperatures produced no effect on the shale. Any heat of friction developed was not enough to solubilize a measurable amount of organic matter. Drying oil shale in vacuum, nitrogen, or air to free it from its natural moisture content caused a loss of soluble organic matter. Of the solvents used, chloroform was the most satisfactory, as it was volatilized without excessive loss of extract. Extraction curves of several oil shales showed that the organic matter was insoluble in common organic solvents. Of the soluble matter derived from oil shales by extraction, 60 to 70 percent consisted of complex fatty acids. In drying extracts to free them of the solvent used, it was almost impossible to prevent some loss of extract by volatilization. Oil shale, when treated with reagents such as H_2SO_4, HCl, NaOH, and NaCl solutions, yielded essentially the same amount of soluble extract as before treatment. Acetic acid caused a slight increase in the solubility of the organic matter; anhydrous aluminum chloride caused a considerable increase. Adsorbents like fuller's earth mixed with oil shale or bitumen derived from oil shale by extraction decreased the solubility of the extractable matter.

106. FERRIS, BERNARD J. Studies of Soluble Material in Oil Shales. Mines Magazine (Colorado Sch. Mines), vol. 38, No. 9, 1948, pp. 19-22; 28.

Soluble organic constituents are dispersed uniformly throughout shale from Rifle (Colo.) and do not necessarily exist as concentrated aggregates in a groundmass of less-soluble material of relatively uniform composition. The greater solubility of the organic matter in oil shale particles of small size is primarily a result of the larger surface area exposed to the leaching action of the solvent. The greatest increase of increment in solubility was between the 30- and 120-mesh screen sizes. The very slight increase in soluble extract between the 120- and 170-mesh screen size indicated an approach toward complete extraction of soluble material from the shale. The solubility of the kerogen (weight-percent of oil shale) in Green River oil shale is (a) an inverse function of particle size and the specific gravity of the oil shale, (b) a direct function of time of exposure to the solvent, (c) a direct function of temperature of the solvent, and (d) a direct function of oil yield.

107. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1949. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 4652, 1950, pp. 59-60.

Oil shale from Rifle (Colo.) was extracted in a Sohxlet-type apparatus by various solvents. Of the solvents tried (ethylene chloride, pyridine, ethylene diamine, dimethyl formamide, tetralin, o-cyclohexyl phenol, and phenanthrene) tetralin was the most effective and dissolved approximately 18 percent of the organic material. The amount of extract obtained was partially dependent upon the extraction temperature. This indicated that thermal degradation, as well as solvent extraction, was involved.

108. FERRIS, BERNARD J. Are Oil Shales Natural Source Beds of Petroleum? Part 2. World Oil, vol. 131, No. 5, 1950, pp. 85-86; 89-90.

The effects of time, catalyst, and radioactivity upon the solubility of kerogen from the Green River formation were determined. No free oil was formed under the following conditions: (a) When oil shale was heated for a total of 28 days at temperatures ranging from 200° to 340° C., (b) when six kerogen-bearing sediments of different geological ages and from diverse geographical locations were heated for 26 days at 80° C., (c) when samples of Green River oil shale mixed with various catalysts were heated at 260° C. for 30 hours, and (d) when a sample of oil shale mixed with carnotite was heated for 1 week at 265° C.

Free oil is not associated with oil shale except where deposits have undergone intense heat from igneous activity or from tectonic movement. It is unlikely that oilfields are related to oil-shale deposits. If petroleum was formed by the conversion of kerogen, ancient oil shales such as the Cambrian Albert series would have been transformed to petroleum long before the present era. Also, a carbonized or graphitic residue would have resulted if petroleum was thermally decomposed from kerogen.

109. SCHNACKENBERG, WERNER D., AND PRIEN, CHARLES H. The Effect of Solvent Properties in Thermal Decomposition of Oil Shale Kerogen. Ind. Eng. Chem., vol. 45, 1953, pp. 313-322.

Finely ground oil shale from Rifle (Colo.) was subjected to thermal solution at 200 C. and at the autogenous pressure of selected associating and nonassociating solvents. The percent kerogen made soluble was determined from the weight of extract. Following are the percentage yields of extracts expressed as percent of Fischer assay: phenol 23.8, dimethylsulfolane 12.6, methanol 13.6, tetralin 49.5, decalin 38.1, benzene 22.1, cyclohexene 24.3, cyclohexane 19.5, acetone 12.9, and n-hexane 17.1.

The total yield of product oil was a function of the molecular volume of the solvent; however, no significant relationship was found between internal pressure of the solvent and product yield. The least amount of pyrolysis (smallest decrease in carbon-hydrogen ratio) was obtained with solvents having the highest internal pressure. Associating solvents produced oils of lower carbon-hydrogen, carbon-nitrogen, and carbon-sulfur ratios (higher percentages of hydrogen, nitrogen, and sulfur per carbon) than the nonassociating solvents. It appeared that the hydrogen-rich portion of the original macromolecules, made soluble by associating solvents, was produced by fission at hetero points (oxygen, nitrogen, and sulfur) in the molecule and dissolved as a result of hydrogen bonding effects.

It was postulated that kerogen exists in at least two different forms. One form, which is rich in hetero atoms, tends to produce polar groups attached to hydrocarbons upon thermal decomposition and is dissolved by associating solvents. The remaining form is predominantly hydrocarbonlike and poor in hetero atoms in relation to carbon.

110. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1954. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 5119, 1955, pp. 93-94.

Tests were made to compare the swelling and exfoliation of oil shale from Rifle (Colo.) by different solvents. Comparable pieces of a 58-gallon-per-ton shale, each measuring 1/2 by 1/2 by 1-1/4 inches, were immersed in solvents for 8 weeks. Chloroform caused the most extensive swelling and exfoliation of the shale (the solvents included chloroform, carbon disulfide, benzene, carbon tetrachloride, tetralin, pyridine, 1,1,2-trichloroethane, tetrachloroethane, trichloroethylene, methylene chloride, water, methanol, methyl cyclo-hexane, n-heptane, and acetone). Acetone, n-heptane, methanol and methyl cyclohexane were the least effective solvents and caused no apparent changes over a period of 2 weeks. Generally, little change occurred after the initial 2 weeks, and the effects were roughly proportional to the solubility of the organic material in the solvents.

111. _____. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1954. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 5119, 1955, pp. 99-100.

Samples of a 66-gallon-per-ton shale from Rifle (Colo.) were treated in a Soxhlet extractor for 24 hours at the boiling point of the solvents and also in a pressure vessel at 200° C. for 30 minutes. The following solvents used were: tetralin, phenol, benzene, methyl alcohol, n-heptane, acetone, dipropylene glycol and Dow polyglycol P-400. No evolution of gas from the organic material was observed, and each of the solvents extracted comparable amounts of organic material by each method. Yields of extract obtained from kerogen ranged from 28 percent for tetralin to 5 percent for acetone. Generally, nitrogenous compounds were extracted to a limited extent only, but polar solvents were more effective in removing nitrogen compounds than nonpolar solvents. Sulfur and oxygen-containing constituents were extracted most effectively by polar solvents; oxygenated compounds were extracted best by methanol. The percentage of oxygen in the methanol extract was approximately twice that of kerogen; whereas, oxygen contents of the other extracts were approximately the same as, or less than, the oxygen content of kerogen.

112. MOORE, J. W., AND DUNNING, H. N. Interfacial Activities and Porphyrin Content of Oil-Shale Extracts. Ind. Eng. Chem., vol. 47, 1955, pp. 1440-1444.

An oil-shale sample from Rifle (Colo.) was extracted successively with solvents of increasing polarity. Interfacial activities as well as porphyrin, nitrogen, and metal contents of the extracts were determined.

Successive extractions with benzene, benzene-methanol mixture, methanol, chloroform-methanol mixture, and pyridine produced 3.70 weight-percent of extract. Changing the order of treatment with methanol and a chloroform-methanol mixture produced 4.19 weight-percent of extract from raw shale.

Infrared absorption peaks at 552 and 396 millimicrons and a weak absorption band at about 515 showed the presence of various amounts of a metal-porphyrin complex in several extracts. The wavelengths of the absorption peaks in the visible region indicated that the metal part of the porphyrin complex was iron or nickel with a major part complexed with iron.

The interfacial activities and film-forming tendencies of the extracts generally paralleled their porphyrin and nitrogen contents. The single exception was the pyridine extract that had a relatively low porphyrin content but high interfacial activity. However, this extract was rich in nitrogen.

Synthesis of an iron-porphyrin complex from the porphyrin aggregate, followed by ferrous acetate spectral studies of this complex, showed the presence of considerable amounts of the iron-porphyrin complex. Several of the oil shale extracts were unusually rich in porphyrin and contained 0.133 to 0.346 weight-percent of porphyrin aggregate.

Degradation Studies[13/]

113. Industrial and Engineering Chemistry. Oyle From a Kind of Stone. vol. 40, No. 12, 1948, pp. 14A-22A.

Oil shale from Rifle (Colo.) was suspended as a thick slurry in tetrahydronaphthalene at various temperatures and hydrogen pressures in the presence of

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[13/] Additional information is presented in items 64, 121, and 181.

catalysts such as tin, nickel, or their sulfides. The carbon-hydrogen ratios of the liquid products decreased with increasing hydrogenation temperature and pressure. The nitrogen content of the gases liberated by cracking reached a minimum at about 200 atmospheres pressure and increased continuously with temperature. Analyses of the gas showed the presence of carbon dioxide, nitrogen, ammonia, hydrogen sulfide, and small quantities of hydrocarbons. The greatest quantity of nitrogen-containing compounds in the liquid and solid products was obtained at low temperatures and decreased as the temperature increased.

114. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1949. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 4652, 1950, pp. 49-50.

Raw shale from Rifle (Colo.) and shale that had been acid-leached to remove mineral carbonates were heated at temperatures ranging from 260° to 538° C. The first gas evolved was carbon dioxide. When retorting raw shale, part of this carbon dioxide may have come from mineral carbonates, but from the acid-leached shale the carbon dioxide must have come from such organic chemical groups as carboxyl, aldehyde, or ketones. The carbon dioxide evolution for acid-treated shale was greatest at 260° C. and decreased with increase in temperature. Evolution of mineral carbon dioxide from raw shale became rapid at approximately 538° C. For both shales, the yield of hydrogen sulfide increased after a shale temperature of about 260° C. had been reached. Possibly at this temperature, reduction of some of the mineral sulfides by hydrogen occurred. Hydrogen, methane, and other hydrocarbons were formed with the oil and were produced at about the same relative rate. Therefore, production of hydrocarbon gases appeared to be closely connected with the reactions that took place to produce oil from the shale organic matter.

115. _____. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1952. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 4943, 1953, pp. 60-62.

A study of the constitution of the organic material in oil shale from Rifle (Colo.) was made by degrading the kerogen into organic acids by alkaline potassium permanganate oxidation. Attempts were made to fractionate the organic acids by the following methods: (a) Separation of the acids according to their solubility in solutions of different pH values; (b) adsorption of the organic acids on silica gel, silicic acid, amberlite resins, florisil, alumina, and paper; (c) fractionation of the silver salts of the acids; and (d) solvent extraction. None of the methods were successful.

The precipitated organic acids (regenerated humic acids) obtained by permanganate oxidation of kerogen were oxidized further by ozone. After 12 hours the ozonized product consisted of 2 percent volatile acids, 28 percent carbon dioxide, 17 percent oxalic acid, 11 percent nonvolatile-nonoxalic acids, and 42 percent unoxidized material. After 100 hours of treatment, the ozonized product consisted of 2 percent volatile acids, 35 percent carbon dioxide, 12 percent oxalic acid, 41 percent nonvolatile-nonoxalic acids, and 10 percent unoxidized material. Although extensive degradation resulted from treatment for 100 hours, the reaction was slow and did not indicate extensive ozonization of double-bond structures. Similar treatment of raw oil shale was even less effective and converted only 19 percent of the organic carbon to water-soluble acids. Hydrogenolysis of the same precipitated acids by Raney nickel in boiling solutions of methanol and dioxane produced only small amounts of degradation products.

116. ROBINSON, W. E., HEADY, H. H., AND HUBBARD, A. B. Alkaline Permanganate Oxidation of Oil-Shale Kerogen. Ind. Eng. Chem., vol. 45, 1953, pp. 788-791.

Samples of oil shale from Rifle (Colo.) and known materials were oxidized by alkaline potassium permanganate. The rate of oxidation and the distribution of organic carbon in the oxidation products were determined. The Colorado kerogen was oxidized nearly to nonbenzenoid water-soluble products in 100 hours. The oxidation behavior of the kerogen appeared to be similar to that of Estonian and Gdov oil shales, as similar oxidation products were obtained from each. Based on these results, aromatic hydrocarbons, condensed aromatic hydrocarbons, and condensed oxygen heterocyclic (unsaturated) structures were scarce in the Colorado kerogen. However, noncondensed heterocyclic rings, noncondensed hydroxy or methoxy substituted benzene rings, aliphatic chains, noncondensed aromatic ethers and aldehydes, noncondensed cyclic ketones (saturated), monocyclic terpenes, or carbohydrates may be present in the kerogen. It was concluded that Colorado kerogen does not consist of condensed benzenoid structures and may be essentially nonbenzenoid.

117. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1953. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 5044, 1954, pp. 46-48.

Some of the properties of n-butyl esters prepared from acids obtained by oxidation of kerogen from Rifle (Colo.) are given. The filtrate-soluble acids were fractionated by solvent treatment with ether, methyl ethyl ketone (MEK), and water. These fractions were converted to n-butyl esters and the esters fractionally distilled. Esters of the ether-soluble acids ranged in molecular weight from 220 to 840, the esters of the MEK-soluble acids from 210 to 930, and the esters of the water-soluble acids from 210 to 1,100. This indicated little or no fractionation by solvent treatment.

Precipitated kerogen acids (regenerated humic acids) were converted to anilides, phenylphenacyl bromides, p-nitrobenzyl esters, and to salts of silver, lead, mercury, strontium, sodium, ammonia, and zinc. None of these derivatives were crystalline.

118. ROBINSON, W. E., CUMMINS, J. J., AND STANFIELD, K. E. Constitution of Organic Acids Prepared From Colorado Oil Shale Based Upon Their N-Butyl Esters. Ind. Eng. Chem., vol. 48, 1956, pp. 1134-1138.

The constitution of the organic acids obtained from kerogen of oil shale from Rifle (Colo.) by alkaline potassium permanganate oxidation was determined.

The acids were converted to n-butyl esters for fractionation and characterization. The crude esters contained approximately 42.4 percent butyl oxalate, 7.1 percent butyl succinate, 6.0 percent butyl glutarate, 1.9 percent butyl adipate, 1.1 percent butyl pimelate, 0.5 percent butyl suberate, 18.2 percent unidentified distillate, and 22.8 percent nondistillable residue.

The esters were of two different types: One was the volatile esters that resulted from extensive degradation of the kerogen and consisted of low-molecular-weight members of the alkane series of difunctional esters. The other was the high-molecular-weight esters, which appeared to be saturated cyclic structures rather than aromatic or straight-chain paraffins.

The production of predominant dicarboxylic acids indicated that kerogen from this shale does not have a highly condensed structure, as the latter yields multifunctional carboxylic acids on oxidation. Therefore, kerogen in Colorado oil shale appeared to be composed of high-molecular-weight substances with saturated rings, which may be partially condensed or connected by short aliphatic chains. The high-molecular-weight acids contained approximately 1 atom of oxygen per molecule in excess of that present as carboxyl groups. This indicated the presence of carbonyl groups, hydroxyl groups, or ether linkages. Presumably, substances of this type would be oxidized progressively by alkaline permanganate into series of saturated dicarboxylic acids of lower molecular weight, until finally the ring structures would be ruptured to yield aliphatic dicarboxylic acids of 6 carbon atoms, or less, plus carbon dioxide.

119. HUBBARD, ARNOLD B., AND FESTER, J. I. Hydrogenolysis of Colorado Oil-Shale Kerogen. Chem. Eng. Data Series, vol. 3, 1958, pp. 147-152.

Preliminary hydrogenolysis tests were made on samples of kerogen concentrate of oil shale from Rifle (Colo.) by treatment with hydrogen at different temperatures and pressures. The following catalysts were used: (a) tungsten nickel sulfide, (b) stannous chloride, (c) stannous chloride plus ammonium chloride, (d) stannous chloride plus ammonium chloride and powdered zinc, (e) Adkins catalyst, (f) nickel chloride, (g) nickel chloride plus powdered zinc, and (h) nickel chloride plus ammonium chloride.

From the preliminary study, it was found that the maximum conversion of kerogen to benzene-soluble material with minimum yield of gas was obtained by stannous chloride with 4,200 p.s.i.g. hydrogen pressure (hot) at 355° C. for 4 hours. Batches of pulverized kerogen concentrate were treated under these conditions, and the soluble products were recovered. The total soluble material was fractionated by solvent treatment, chromatography, fractional crystallization, vacuum distillation, formation of complexes, and acid and base extractions.

The hydrogenolysis product consisted of 7.6 percent gas, 80.0 percent benzene-soluble material, 5.6 percent trichloroethylene-soluble material, and 6.8 percent insoluble residue. Approximately 90 percent of the kerogen nitrogen and sulfur and over 80 percent of the kerogen oxygen were eliminated as gas and residue and were not recovered in the soluble products. The benzene-soluble material contained 16 percent wax, 29 percent wax-free oil, 10 percent high-molecular-weight hydrocarbons (containing some oxygen derivatives), 33 percent complex nitrogen and oxygen compounds, and 12 percent other fractions. The wax fraction consisted of straight-chain paraffins having molecular weights of 254 to 441, and branched-chain hydrocarbons and cyclic compounds with molecular weights of 253 to 740. The nitrogen fractions contained 24 to 50 percent basic nitrogen. Infrared analyses of these fractions indicated the presence of aromatic nuclei, condensed structures, short carbon chains, and carbonyl groups. The trichloroethylene-soluble fraction appeared to contain long chains, carbonyl groups, ether linkages, and possible amides.

Low-Temperature Pyrolytic Products[14]

120. FRANKS, ARTHUR J., AND GOODIER, B. D. Preliminary Study of the Organic Matter of Colorado Oil Shales. Colorado Sch. Mines Quart., vol. 17, No. 4, supp. A, 1922, 16 pp.

Samples of air-dried oil shale from Grand Valley (Colo.) were extracted with carbon disulfide. The shale residue was then heated at 300° C. for 4 hours followed by extraction with carbon disulfide to remove soluble material. This process was repeated a number of times. After the first two heating periods, the temperature was raised to 325° C., and for the seventh period the temperature was increased to 350° C. After 16 heating periods, when no further bitumen was formed, the temperature was raised to 375° and 400° C. for two additional periods. The final residue was slowly distilled; and the water, gas, spent shale, and oil were determined. A comparable air-dried, raw-shale sample was distilled, and analyses of the products were determined for comparison. Bitumens formed at 300°, 325°, and 350° C. were combined in proportions based on percent yield and were distilled to dryness.

The series of treatments resulted in a gradual but definite change in the shale. The shale gradually darkened upon heating, and the final residue was black and friable. Small quantities of gas were evolved and had a sulfurous odor. Water was continually evolved, but no evidence of volatile oil was observed. It was possible to convert all oil-forming constituents of the Colorado shale to a soluble product without producing volatile oil.

Indications were that conversion of kerogen to a soluble product resembled slow "cracking" rather than depolymerization, and the soluble bitumen may be formed at temperatures as low as 200° C. (very slowly). These results disagree with conclusions by McKee and Lyder that soluble bitumen is formed at a definite temperature between 400° and 410° C. Within certain limits, the amount of bitumen produced varied almost directly with the time of heating.

The decomposition resulted in a loss of nitrogen. If the kerogen had depolymerized during the decomposition, the percentages of nitrogen in the bitumen and kerogen would have been the same. Data from the distillation of the residue suggested that kerogen consists of two distinct types of materials —an oil-forming constituent of which bitumen is the primary decomposition product and a coke-forming constituent, which yields the fixed carbon of the residue. It was also shown that the part of the kerogen that yielded oil was not a single substance or compound but a complex mixture.

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[14] Additional information is presented in items 6, 19, 59, 62, 64, 68, 72, 109, and 114.

121. CARLSON, ANDERS J. Inorganic Enviroment in Kerogen Transformation. Univ. California Press, Berkley, Calif., 1937, pp. 295-342.

Samples of oil shale from Colorado, Utah, and Kentucky were heated in sealed tubes at temperatures of 250°, 300°, and 350° C. for periods up to 120 hours. The product gases were hydrogen sulfide, carbon dioxide, hydrogen, methane, ethane, and nitrogen, with smaller amounts of unsaturates, carbon monoxide, and heavier paraffins. The trends of the gas volumes and compositions with respect to period of heating indicated two stages of gas formation. During the initial stage, gas formation was due to the decomposition of kerogen; whereas, the second stage was attributed to cracking of the bitumen formed.

The rate of kerogen conversion decreased as the proportion of inorganic matter decreased, which suggests that at least some of the inorganic constituents take an active part in the transformation. An important part of the mechanism may consist of the destruction of a combination (an adsorption phenomena or chemical combination) between the organic and inorganic constituents. The conversion to soluble products appeared to be a first-order reaction.

Kerogen structure may consist of long-chain fatty acids combined with an inorganic base. The presence of carboxyl groups was indicated by the production of carbon dioxide in the absence of air and at the temperatures employed. Removal of the inorganic matter with weak acids did not degrade the kerogen, but it did alter the molecular structure so as to make it less readily converted to soluble products by heat. It was surmised that slow evolution of bitumen from kerogen takes place in oil shale at natural rock temperatures and the soluble material present in kerogen was formed since deposition.

122. PRINGLE, JOHN W., BARRICK, PAUL L., AND WIGTON, HENRY F. Vacuum Retorting of Oil Shale in a Fluidized Bed. Ind. Eng. Chem., vol. 44, 1952, pp. 1489-1491.

Samples of oil shale from the Green River formation of Colorado were retorted in a bed fluidized by nitrogen gas at temperatures of 330° to 410° C. for 25 to 50 minutes and pressures of 5 to 600 mm. mercury. A heavy oil (semisolid material with a melting point from 29° to 32° C.) was collected by an air-cooled condenser, while a light fluid and some water were condensed in a dry-ice trap. The heavy oil had an average density of 0.94 at 27° C., a molecular weight of about 400, and a chemical composition of approximately 81 percent carbon, 11 percent hydrogen, and 0.5 percent sulfur. Based on this molecular weight, the oil absorbed 1.2 moles of iodine per mole of oil. The shale residue was extracted with methyl ethyl ketone after each heating test to determine the amount of soluble oil formed.

From the iodine absorption and the carbon-hydrogen ratio, it was concluded that the heavy oil produced by vacuum retorting at low temperature was of olefinic and cyclic character. The high initial boiling point may indicate that this oil contained larger fragments of the parent organic material present in the oil shale than the oil obtained by other retorting methods.

123. BUREAU OF MINES. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1955. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations 5237, 1956, pp. 66-67.

Oil shale from Rifle (Colo.) assaying 66 gallons of oil per ton, was heated at 340° C. in the presence of tetralin for five successive periods (one 0.5-hour period plus four 24-hour periods) to determine if the organic material rendered soluble during one period resembled that formed in succeeding periods. After each heating period, the tetralin-soluble material was removed and the insoluble residue was then subjected to further treatment. Other samples of oil shale were treated with tetralin at 100° to 350° C. to determine the effect of temperature on the initial thermal products of kerogen. The extracts were separated into four fractions: Pentane-insoluble asphaltenes, pentane-soluble oil, pentane-soluble resins, and pentane-soluble waxes.

The molecular weights of the extracts were of the same order of magnitude and indicated that soluble products obtained by the successive heat treatments were of the same general type. The ratios of hydrogen, oxygen, sulfur, and nitrogen to carbon of the extracts were less than for the original kerogen, but the oxygen-carbon ratios were not as low as that of the assay oil normally obtained from kerogen. Eighty-six percent of the kerogen was removed from the oil shale after 96-1/2 hours of treatment.

Composition of Shale Oil

124. BOTKIN, C. W. A Study of the Saturated and Unsaturated Oils From Shale. Chem. Met. Eng., vol. 24, 1921, pp. 876-880.

Shale oils prepared from oil shales of Quebec, England, Scotland, Colorado, Wyoming, Utah, and Nevada were studied to determine the extent and cause of unsaturation, distribution of saturates, effect of cracking on unsaturation, and some of the properties of the unsaturated products. Colorado shale oil contained 11.6 to 28.0 percent saturates. None of the retorting conditions used produced more than 30 percent saturates, and the smallest amount was produced when steam retorting was used to minimize cracking. Insufficient organic hydrogen is present in kerogen to produce saturated compounds with all of the carbon; consequently, for maximum yield the oil must be highly unsaturated. Decomposition occurred during redistillation of the shale oil and was accompanied by a considerable increase in the saturation of the oil.

125. FRANKS, ARTHUR J. Studies in Colorado Shale Oil. Chem. Met. Eng., vol. 24, 1921, pp. 561-564.

Oil Shale from DeBeque (Colo.) was pyrolyzed in a Ginet retort under low-temperature carbonization conditions. The crude shale oil was fractionated after which the distribution and character of the saturated, unsaturated, sulfur, and nitrogen compounds were determined. Generally, cracking of the unsaturated and unstable oils in the heavy-distillate fraction produced lower-molecular-weight oils of higher saturation.

126. _____. Studies of Colorado Shale Oil. II. Chem. Met. Eng., vol. 25, 1921, pp. 49-53.

Simultaneous loss of nitrogen and sulfur, with increase in saturation due to cracking heavy fractions of Colorado shale oil from oil shale near DeBeque (Colo.), indicated that unsaturated and unstable material was degraded to form saturated compounds. This unsaturated material was comprised of a number of unstable compounds of high molecular weight that were rich in nitrogen, sulfur, and oxygen. It is possible that the initial unstable substances disintegrated, then recombined to form more stable compounds.

127. _____. Studies of Colorado Shale Oil. III. Chem. Met. Eng., vol. 25, 1921, pp. 731-735, 778-782.

Samples of shale oil from DeBeque (Colo.) were redistilled at atmospheric pressure. The low-molecular-weight fractions were very stable and were not altered to any appreciable extent by redistillation; however, the heavy fractions were unstable. Each distillation produced gas, decreased the weight and volume of oil recovered, increased the stability of the distillate, lowered the specific gravity of the oil, decreased the sulfur and nitrogen content of the oil, and increased the amount of saturated hydrocarbons in the distillate. The heavy, unsaturated bitumens were the source of the new saturated compounds.

The secondary products consisted of paraffins and olefins and smaller amounts of organic sulfur and nitrogen compounds, aromatics, and diolefins. The heavy, unstable bitumens were very complex substances, which contained sulfur, nitrogen, and oxygen, but almost no saturated hydrocarbons.

A theory was presented to explain the formation of oil from Colorado oil shale. Heat causes a depolymerization or some similar transformation of the kerogen to a less complex, heavy, unstable, and unsaturated material, which in turn decomposes to a varying degree with the formation of stable products of a lower molecular weight. This secondary decomposition accounts for the presence of low-molecular-weight constituents found in crude shale oils.

128. BOTKIN, C. W. Relation of Shale-Oil Residue to Other Bitumens. Chem. Met. Eng., vol. 26, 1922, pp. 445-448.

Destructive distillations were made on shale-oil residues (from Colorado and Utah oil shales) and on gilsonite, grahamite, asphalt, and rosin. The products were then compared. Gilsonite proved to be almost identical in properties to the shale-oil residue, and their distillation products were also similar in quantity and properties. Destructive distillation of asphalt yielded less oil and a much lower percentage of saturates than the shale-oil residue, but the distribution of the saturates in the oils was similar. On distillation of the rosin, saturates were formed and were nearly equal in quantity to those obtained from crude oil The decomposition was accompanied by the formation of a much larger quantity of water and the distribution of the saturates in the oil was not the same as shale oil. The shale-oil bitumen was more closely related in composition and properties to gilsonite than it was to asphalt, grahamite, or petroleum residue.

The high content of nitrogen in the shale-oil residue and the large nitrogen losses, which occurred when the shale oil and gilsonite were redistilled, indicated that the decomposition and increase in saturates was probably caused by the secondary cracking of heavy nitrogen compounds.

The saturates in the oil from rosin, gilsonite, and shale-oil residue are not present as such in the parent substance, but are produced by decomposition when these substances are destructively distilled at atmospheric pressure.

129. STAUFFER, JOHN C. The Nitrogen Compounds of Colorado Shale Oil. Thesis of Columbia Univ., New York, N. Y., 1926, 63 pp.

The nitrogen bases of Colorado shale oil from oil shale near DeBeque (Colo.) that distilled below 300° C. were principally tertiary amines of the pyridine homolog type. Fractions boiling below 300° C. contained symmetrical collidine and 2-methyl 5-ethyl pyridine but no quinoline or isoquinoline. The higher-boiling tertiary amines contained longer substituted side chains and were partially unsaturated. Secondary amines, which corresponded to the substituted pyrroles and piperidines, were present in the crude bases. There was also a trace of acid nitriles present; however, primary amines were not present in amounts greater than 1 percent. The composition of the nitrogen bases boiling below 300° C. resembled those of low-temperature coal tar, except for the absence of quinolines, isoquinolines, hydrogenated quinolines, and hydrogenated isoquinolines.

130. GUTHRIE, BOYD. Nitrogen and Its Compounds in Oil Shale and Shale Oil. Ch. 9 in Studies of Certain Properties of Oil Shale and Shale Oil. Bureau of Mines Bull. 415, 1938, pp. 123-151.

J. W. Horne, W. L. Finley, and C. P. Hopkins studied the distribution of of nitrogen in retorted products from Colorado oil shale (from DeBeque, Colo.). The percentage of nitrogen in the oils was lower at slow rates of retorting than at faster rates. The nitrogen content of the oil was highest in the heavy distillate, whereas the percentage of sulfur was slightly higher in the light distillate. Ammonia was liberated during all stages of pyrolysis; hydrogen sulfide was produced principally between 350° and 465° C.

Pyrolysis altered the unsaturated nitrogen compounds to more stable compounds such as pyridine homologs and ammonia. Other pyrolysis products were carbonates, sulfides, sulfites, thiosulfates, and phenolic homologs. The oily basic compounds were tertiary amines and included two isomers of picoline, two isomers of lutidine, three isomers of collidine, and one isomer of parvoline.

131. BALL, JAMES O. Survey of Bitumen Analyses and Extraction Methods. Colorado Sch. Mines Quart., vol. 39, No. 1, 1944, p. 82.

R. D. Locke and W. E. Laspe analyzed shale oil (author's note - presumably from Colorado oil shale) in petroleum laboratories at the Colorado School of Mines.

The asphalt fraction had the following composition: asphaltenes, 47.5 percent; resins, 28.5 percent; oils, 20.0 percent; and wax, 4.0 percent. The shale-oil naphtha had the following properties: 47.0° API gravity, 152° F. initial boiling point at 625 mm. Hg, 440° F. maximum boiling point at 625 mm. Hg, and 61 octane number. Although the wax content of the shale oil depended somewhat upon the method of retorting, the yield of wax ranged from 2 to 6 percent of the crude oil. The amount of asphaltic material varied with the method of retorting and ranged from 2.5 to 5.6 percent of the crude oil.

132. BALL, JOHN S., DINNEEN, G. U., SMITH, J. R., BAILEY, C. W., AND VAN METER, ROBIN. Composition of Colorado Shale-Oil Naphtha. Ind. Eng. Chem., vol. 41, 1949, pp. 581-587.

Shale-oil naphtha produced from oil shale of Rifle (Colo.) by retorting in a Pumpherston unit was separated into neutral naphtha, tar acids, and tar bases. The composition of the naphtha represented about 20 percent of the crude and may be summarized as follows: tar acids, 0.8 percent; tar bases, 5.6 percent; paraffins, 21.2 percent; naphthenes, 8.2 percent; aliphatic olefins, 25.9 percent; cyclic olefins, 15.1 percent; aromatics, 18.2 percent; sulfur compounds, 3.4 percent; nitrogen compounds (other than tar bases), 0.9 percent; and separation loss, 0.7 percent. The composition of the paraffins in the neutral Pumpherston naphtha was as follows: n-hexane, 0.1 percent; methyl hexanes, 0.2 percent; n-heptane, 0.2 percent; dimethylhexanes, 0.3 percent; methylheptane, 0.2 percent; n-octane, 1.6 percent; dimethylheptane, 0.6 percent; methyloctanes, 0.5 percent; n-nonane, 3.4 percent; C_{10}-hexanes, heptanes, and octanes, 1.7 percent; methylnonanes, 0.5 percent; n-decane, 4.1 percent; and residue, 9.3 percent. The composition of the naphthenes in the neutral Pumpherston naphtha was as follows: C_6 naphthenes, 0.03 percent; methyl cyclohexane, 0.03 percent; ethyl cyclohexane, 0.04 percent; 1,2,4-trimethylcyclopentane, 0.1 percent; other C_8 naphthenes, 0.7 percent; C_9 naphthenes 2.1 percent; C_{10} naphthenes, 1.6 percent; and residue, 4.2 percent. The aromatics of the neutral Pumpherston naphtha had the following composition: benzene, 0.2 percent; toluene, 1.1 percent; ethylbenzene, 0.3 percent; p-xylene, 0.7 percent; m-xylene, 1.6 percent; o-xylene, 0.9 percent; 1-methyl-3-ethylbenzene, 0.8 percent; 1-methyl-4-ethylbenzene, 0.4 percent; 1-methyl-2-ethylbenzene and 1,3,5-trimethylbenzene, 0.9 percent; 1,2,4-trimethylbenzene, 1.5 percent; 1-methyl-2-isopropylbenzene, 1-methyl-3-isopropylbenzene, and 1-methyl-4-isopropylbenzene, 1.8 percent; and residue, 9.2 percent. The composition of the aliphatic olefins in the neutral Pumpherston naphtha was as follows: n-heptenes, 0.7 percent; n-octenes, 2.5 percent; branched nonenes, 1.1 percent; n-nonenes, 4.2 percent; branched decenes, 1.9 percent; and n-decenes, 4.3 percent. The cyclic olefins in the neutral Pumpherston naphtha had the following composition: C_6 cyclic olefins, 0.1 percent; C_7 cyclic olefins, 0.5 percent; C_8 cyclic olefins, 1.4 percent; C_9 cyclic olefins, 3.2 percent; and C_{10} cyclic olefins, 2.6 percent. Phenol and p-cresol were identified in the tar acid fraction, and 2-methylpyridine, 2,4,6-trimethylpyridine, quinoline, and 2-methyl-quinoline were identified in the tar base fraction.

133. TISOT, P. R., AND HORNE, JOSEPH W. Waxes From Shale-Oil Wax Distillate. Bureau of Mines Rept. of Investigations 4708, 1950, 21 pp.

Shale-oil waxes were separated by distillation from crude shale oil (from Rifle, Colo., oil shale) previously topped to 675° F. at 585 mm. Hg pressure. The wax distilled at an overhead temperature of 525° F. at 5 mm. Hg pressure. Three grades of shale-oil wax were made and designated as crude, semirefined, and fully refined. Properties and compositions of the waxes were determined. Methyl ethyl ketone at 32° F. was used for dewaxing, and a total of 18.8 percent of the wax distillate (6.6 percent of the crude shale oil) was obtained by this treatment. Quantitative and qualitative analyses for hydrocarbon groups in the waxes were determined by silica gel adsorption. The crude wax contained 83.3 percent paraffins and naphthenes and 16.7 percent olefins. The semirefined wax contained 87.4 percent paraffins and naphthenes, and 12.6 percent olefins, whereas the refined wax was 100 percent paraffins and naphthenes. Ultraviolet spectra of the waxes also indicated that no aromatic structures were present. The crude wax contained 0.03 percent sulfur but no nitrogen. Physical properties of the waxes were determined for evaluation purposes.

134. JANSSEN, A. G., SCHIERZ, E. R., VAN METER, R., AND BALL, JOHN S. Isolation and Identification of Pyrrole and 2-Methylpyrrole From Shale Oil. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 4040-4041.

The shale oil studied was produced from Rifle (Colo.) oil shale in an N-T-U retort. Material boiling up to 195° C. was separated by distillation, and the tar acids were removed by dilute NaOH. Pyrroles were then separated as potassium pyrroles by refluxing the naphtha over solid KOH. The potassium compounds were washed with pentane and hydrolyzed. The recovered oil was distilled and derivatives were made from the fractions. Phthalic anhydride and tetraiodo derivatives of pyrrole were isolated and compared with authentic samples. The ketoxime derivatives of 2-methyl-pyrrole were prepared from the fractions.

The shale oil contained pyrrole and 2-methylpyrrole. However, this work did not exclude the possible presence of other 1-substituted pyrroles or other lower-boiling 1-methylpyrroles.

135. KOMMES, W. C., AND STANFIELD, K. E. Properties of Shale-Oil Asphalts from Colorado Oil Shale. Proc. Assoc. Asphalt Paving Technol., vol. 20, 1951, pp. 473-489.

Asphalts from N-T-U crude oil of Green River oil shale at Rifle (Colo.) were prepared by vacuum distillation, propane precipitation, air-blowing, and by thermal cracking of the crude oil, and were then evaluated according to commercial specification tests. A 116 penetration (at 77° F.) asphalt, prepared by vacuum distillation and representing 17 percent of the crude oil, contained 85.02 percent carbon, 10.24 percent hydrogen, 2.82 percent nitrogen, 0.56 percent sulfur, and 1.36 percent oxygen (by difference). A similar asphalt of 173 penetration contained 15 percent asphaltenes, 47 percent resins, and 38 percent oils. The nitrogen contents of these constituents increased with increasing molecular weight; the oils contained 1.1 percent nitrogen, resins 3.4 percent, and asphaltenes 4.5 percent.

136. CADY, WILLIAM E., AND SEELIG, HERMAN S. Composition of Shale Oil. Ind. Eng. Chem., vol. 44, 1952, pp. 2636-2641.

N-T-U shale oil from Rifle (Colo.) oil shale was examined by distillation, extraction with a metal chloride in concentrated HCl, absorption, extractive crystallization with urea, and infrared spectrometry.

The shale oil consisted of 6 percent n-paraffins, 6 percent n-olefins, 5 percent isoparaffins plus naphthenes, 12 percent iso-olefins plus cyclo-olefins, 4 percent monocyclic aromatics, 6 percent polycyclic aromatics, 36 percent nitrogen compounds, 6 percent sulfur compounds, and 19-percent oxygen compounds.

The iso and cyclic olefinic and paraffinic content of the shale-oil fractions decreased as the nitrogen content increased. This suggested that the yield of iso plus cyclic compounds depended primarily upon the denitrogenation of nitrogen compounds, and this denitrogenation was less complete for compounds of higher molecular weight. However, in the higher boiling half of shale oil, an unexpected increase in isoparaffins plus naphthenes (cyclo paraffins) and a decrease in iso-olefins plus cyclo-olefins and in polycyclic aromatics suggested that the degradation of the nitrogen compounds originally formed from kerogen during retorting was as follows: nitrogen compounds → isoparaffins plus naphthenes → iso-olefins plus cyclo-olefins → aromatics. The results also suggested that the polycyclic naphthenes of higher molecular weight did not dehydrogenate as readily as those of lower molecular weight. The constancy of the hydrocarbon composition of the lower boiling half of the shale oil suggested that kerogen consists predominantly of homologs of a complex structure, which upon degradation yields hydrocarbons having the same distribution of structural types.

137. DINNEEN, G. U., SMITH, J. R., AND BAILY, C. W. High Temperature Shale Oil-Product Composition. Ind. Eng. Chem., vol. 44, 1952, pp. 2647-2650.

Oil shale from Rifle (Colo.) was retorted at temperatures substantially higher than those normally employed. The oil obtained by retorting at 1,500° to 1,700° F. (816° to 927° C.) was highly aromatic and contained almost negligible quantities of saturates and olefins. The 1,200° F. (649° C.) oil, although much less aromatic than the oils produced at the higher temperatures, had about twice the aromatic content of oils produced by the usual retorting methods. The content of benzene and naphthalene increased with temperature of retorting, whereas the content of toluene and methylnaphthalene reached a maximum in the 1,500° F. oil. Other alkylbenzenes of this molecular-weight range were scarce in the 1,700° F. oil and were present in only small amounts in the 1,200° and 1,500° F. oils. Styrene and indene followed the same pattern as the alkylbenzenes. Phenol, o-cresol, and m-cresol were the predominant compounds in the tar acids from the 1,500° F. oil. The tar bases from this oil showed large relative quantities of 2,4,6-trimethylpyridine and 2,4-dimethylpyridine.

138. KINNEY, I. W., JR., SMITH, J. R., AND BALL, JOHN S. Thiophenes in Shale-Oil Naphtha. Anal. Chem., vol. 24, 1952, pp. 1749-1754.

Approximately 80 percent of the total sulfur in a 210° C. end-point naphtha, obtained from oil shale of Rifle (Colo.) appeared to be thiophenic. The compounds identified indicated a definite substitution pattern: 2-monosubstituted predominated over 3-monosubstituted thiophenes; 2,5-disubstituted predominated over other disubstituted thiophenes; and 2,3,5-trisubstituted predominated over 2,3,4-trisubstituted thiophenes. Hydrogenation of 15 of the 17 compounds isolated produced normal alkanes or monomethyl alkanes, all of which were abundant in shale oil. This suggested that thiophenes in shale oil may have been formed by a reversal of this mechanism; that is, dehydrogenation of alkanes followed by cyclization in the presence of sulfur.

The following 17 thiophenes were identified in Colorado shale-oil naphtha: thiophene, 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 3-ethylthiophene, 2,3-dimethylthiophene, 2,5-dimethylthiophene, 3,4-dimethylthiophene, 2-isopropylthiophene, 2-methyl-5-ethylthiophene, 2,3,5-trimethylthiophene, 2-methyl-5-isopropylthiophene, 2-methyl-5-n-propylthiophene, 2,3-dimethyl-5-ethylthiophene, 2,4-dimethyl-5-ethylthiophene, 2-methyl-5-sec. butythiophene, and 2,3-benzothiophene.

139. VAN METER, R. A., BAILEY, C. W., SMITH, J. R., MOORE, R. T., ALLBRIGHT, C. S., JACOBSON, I. A., JR., HYLTON, V. M., AND BALL, J. S. Oxygen and Nitrogen Compounds in Shale-Oil Naphtha. Anal. Chem., vol. 24, 1952, pp. 1758-1763.

Various classes of nitrogen- and oxygen-containing compounds were identified in shale-oil naphtha from Rifle (Colo.) oil shale.

The phenols identified were: phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol, 2-ethylphenol, 4-ethylphenol, and 2,4,6-trimethylphenol.

Pyridines identified were: pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 3,4-dimethylpyridine, 2,3,5-trimethylpyridine, 2,3,6-trimethylpyridine, 2,4,6-trimethylpyridine, 2-methyl-4-ethylpyridine, 2-ethyl-4-methylpyridine, 2,3,4,6-tetramethylpyridine, 2,6-dimethyl-4-ethylpyridine, and 2,4-dimethyl-6-ethylpyridine.

Additional nitrogen and oxygen compounds identified were: 2,3,4,5-tetramethylpyrrole, 2,4,5-trimethyl-3-ethylpyrrole, benzonitrile, 2-methylbenzonitrile, 3-methylbenzonitrile, and benzofuran.

140. CAHNMANN, H. J. Detection and Quantitative Determination of Benzo [a] pyrene in American Shale Oil. Anal. Chem., vol. 27, 1955, pp. 1235-1240.

An investigation was made of carcinogenic constituents in Colorado shale oil. A distillate with a boiling point between 400° to 510° C. was fractionated on Florisil, activated alumina, and silica gel. The shale oil contained 0.003 to 0.004 percent benzo [a] pyrene. This compares with 0.3 to 0.8 percent in coal tar, 0.01 percent in Scottish shale oil, 0.0003 percent in dried sewage humus, and 0.00002 percent in cigarette tar.

141. LOCHTE, H. L., AND MEYER, H. W. H. Some Colorado Shale-Oil Bases. Jour. Am. Chem. Soc., vol. 78, 1956, pp. 2150-2153.

Light gas-oil distillate from Rifle (Colo.) shale oil was treated with 4 N NaOH to remove acidic compounds, then with dilute H_2SO_4 to extract the basic compounds liberated by NaOH. The bases were fractionated by distillation into 227° to 239° C. and 264° to 300° C. boiling-range fractions.

The 227° to 239° C. boiling-range fraction contained quinoline, isoquinoline, and a series of methyl homologs. The 264° to 290° C. boiling-range fraction contained 2,3,8-trimethylquinoline but did not contain the very stable $C_{16}H_{25}N$ base found in California petroleum bases. Generally, these shale-oil bases formed much larger amounts of tar residue than did corresponding California petroleum base fractions.

142. DINNEEN, G. U., ALLBRIGHT, C. S., AND BALL, JOHN S. Comparison of Brazilian and Colorado Shale Oils. Chem. Eng. Data Series, vol. 2, 1957, pp. 91-95

Oils from Brazilian and Colorado oil shales were analyzed and the results compared. Colorado shale oil contained about twice as much nitrogen as Brazilian shale oil. This difference was attributed primarily to variations in the structure of the oil-shale kerogens. Oils produced from the two shales by the same method showed regular differences in hydrocarbon composition; the Colorado shale oil had a greater content of saturates and a lower content of aromatic compounds. Colorado shale oil also contained more residuum.

Miscellaneous

143. ANDERSON, VICTOR C. Oil Shale. Colorado Sch. Mines Quart., vol. 18, No. 1, supp. B, 1923, 28 pp.

144. BALL, JAMES O. Oil Shales of the West. Compressed Air Magazine, vol. 50, 1945, pp. 156-160.

145. BOTKIN, C. W. Composition of Oil Shale and Shale Oil. Colorado Sch. Mines Quart., vol. 14, No. 4, 1919, pp. 16-17.

146. BUREAU OF MINES. Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act, 1945, 44 pp.; 1946, 82 pp.; 1947, 128 pp.

147. _____. Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1948. Part II. Oil From Oil Shale. Bureau of Mines Rept. of Investigations (R. I.), 4457, 1949, 56 pp.; R. I. 4652, 1950, 70 pp.; R. I. 4771, 1951, 88 pp.; R. I. 4866, 1952, 86 pp.; R. I. 4943, 1953, 70 pp.; R. I. 5044, 1954, 55 pp.; R. I. 5119, 1955, 115 pp.; R. I. 5237, 1956, 80 pp.

148. DINNEEN, G. U. Shale Oil - What is it? Petrol. Refiner, vol. 33, No. 2, 1954, pp. 113-116.

149. DINNEEN, G. U., BALL, JOHN S., AND THORNE, H. M. Composition of Crude Shale Oils. Ind. Eng. Chem., vol. 44, 1952, pp. 2632-2635.

150. FIELDNER, A. C., AND FISHER, PAUL. Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas. Bureau of Mines Inf. Circ. 7304, 1945, 18 pp.

151. FRANKS, A. J. Colorado Shale Oils. Chem. Met. Eng., vol. 25, 1921, pp. 778-782.

152. GEORGE, R. D. Kerogen of Colorado Oil Shale. Jour. Colorado-Wyoming Acad, Sci., vol. 1, No. 1, 1929, pp. 57-58.

153. HARDING, E. P., AND DUMKE, W. H. Distribution of Sulfur in Oil Shale. II. Ind. Eng. Chem., vol. 20, 1928, p. 164.

154. McKEE, R. H. Shale Oil. Ind. Eng. Chem., vol. 14, 1922, pp. 847-849.

155. POPHAM, F. J. Shale - Some New Reactions. Ind. Chemist, vol. 5, 1929, pp. 269-272.

156. PRIEN, C. H. Oil Shale and Shale Oil. Ch. in Oil Shale and Cannel Coal. The Institute of Petroleum, London, vol. 2, 1951, pp. 76-111.

157. _____. Pyrolysis of Coal and Shale. Ind. Eng. Chem., vol. 40, 1948, pp. 1649-1659; vol. 41, 1949, pp.1906-1914; vol. 42, 1950, pp. 1731-1739; vol. 43, 1951, pp. 2006-2015; vol. 44, 1952, pp. 2064-2072; vol. 45, 1953, pp. 2022-2034; vol. 46, 1954, pp. 1881-1888; vol. 47, 1955, pp. 1911-1915; vol. 48, 1956, pp. 1653-1657; vol. 49, 1957, pp. 1548-1552.

158. SHULTZ, E. B. Pyrolysis of Crude Shale Oil. Ind. Eng. Chem., vol. 47, 1955, pp. 2479-2482.

159. STANFIELD, K. E., AND THORNE, H. M. Oil Shale Research and Process Development. Ind. Eng. Chem., vol. 43, 1951, pp. 16-20.

160. THORNE, H. M., MURPHY, W. I. R., BALL, J. S., STANFIELD, K. E., AND HORNE, J. W. Characteristics and Utilization of Oil Shale and Shale Oil. Ind. Eng. Chem., vol. 43, 1951, pp. 20-27.

161. THORNE, H. M., MURPHY, W. I. R., STANFIELD, K. E., BALL, J. S., AND HORNE, J. W. Green River Oil Shale and Products. Ch. in Oil Shale and Cannel Coal. The Institute of Petroleum, London, vol. 2, 1951, pp. 301-344.

CONSTITUTION AND PROPERTIES OF OTHER OIL-SHALE KEROGENS

162. ROBERTSON, JOHN B. A Chemical Examination of the Organic Matter in Oil Shales. Proc. Roy. Soc. (Edinburgh), vol. 34, 1914, pp. 190-201.

The analyses of Broxburn (Scotland), Pumpherston (Scotland), Armadale (Scotland), Australian, and Knightsbridge oil shales were given. Also, the action of nitric acid and solvents on some of the oil shales was determined.

Carbon-hydrogen ratios of the oil shales varied from 6 to more than 8, and the shales with the lowest ratio (most hydrogen per carbon) produced the largest amount of oil from a given amount of organic matter. There was little resinous material in the oil shales, and most of the organic matter was insoluble in organic solvents.

Nitric acid oxidized Australian torbanite, Broxburn shale, New Battle cannel coal (Scotland), and Glenfullock peat to organic acids. The hydrogen content of the organic acids obtained by oxidizing the following materials increased from ordinary coal to cannel coal to peat to Broxburn shale to torbanite.

The organic substance in oil shale is a decomposition product of vegetable matter similar to that found in peat and cannel coal, and it was produced by a definite combination of external conditions.

163. BLACKBURN, CHESTER OKLAHOMA. Investigation of Oil Shale Kerogen by the Fractionation of the Primary Bitumen in High Vacuum and by Organic Extraction. Colorado Sch. Mines Quart., vol. 19, No. 2, 1924, pp. 9-46.

Oil shale from Elko (Nev.) was pyrolyzed in a partial vacuum, and the products were examined. Retorting in a partial vacuum reduced the amount of cracking and increased the oil yield; the first drop of light oil appeared at 192° C. and the first drop of semisolid bitumen appeared at 232° C.

Oil-shale kerogen from Elko (Nev.) appeared to be a polymerized product of montan wax, which, upon thermal decomposition, depolymerized into primary bitumen and finally into secondary products. Heptocosane ($C_{27}H_{56}$) was extracted from the primary bitumen.

164. McKINNEY, J. W. The Constitution of Kerogen. Jour. Am. Chem. Soc., vol. 46, 1924, pp. 968-979.

Oil shale from the Albert mines in New Brunswick was extracted in a percolation-type extractor with acetone. The extracted oil was separated into asphaltenes, resins, and hydrocarbons. Since asphaltenes and resins were present in small amounts (10 to 5 percent, respectively) only the hydrocarbons were examined. The hydrocarbon fraction was distilled at 1 mm. Hg pressure at temperatures of 50° to 290° C., and the fractions were purified by washing with concentrated H_2SO_4 and dilute NaOH solution. Ultimate analyses, molecular weights, refractive index, and specific gravity were determined for each fraction. Identification of specific compounds was based on these properties.

Twenty-eight compounds belonging to the paraffin, naphthene, and hydronaphthalene series were identified. The hydrocarbons ranged from $C_{14}H_{30}$ to $C_{26}H_{54}$ and $C_{12}H_{24}$ to $C_{24}H_{48}$ plus $C_{25}H_{48}$ and $C_{26}H_{50}$.

165. KOGERMAN, PAUL N. (On the Chemistry of the Estonian Oil-Shale Kukersite.) Arch. Naturkunde Estlands, vol. 10, 1931, pp. 6-27; 37-47; 66-68; 73-75; 82-85.

Estonian oil shale is one of the oldest and richest oil shales in the world. The deposits occur in the Middle-Ordovician strata having a total thickness of 2.2 meters. The ultimate composition of the kerogen varied within the following limits: carbon 76.5 to 76.7 percent, hydrogen 9.1 to 9.2 percent, nitrogen 0.2 to 0.4 percent, sulfur 1.6 to 2.2 percent, chlorine 0.5 to 0.7 percent, and oxygen (by difference) 11.2 to 12.2 percent. The composition of kukersite kerogen corresponds nearly to the empirical formula $(C_8H_{11}O)n$.

One of the most significant differences between kukersite, coal, and lignite is the amount of alkali-soluble substances present. Kukersite has almost no humic acids. In the peat to anthracite series the alkali-soluble substances diminish as the content of carbon increases, but for kukersite, the carbon content has no relation to solubility in potassium hydroxide solution at 230° to 240° C. The shale yields only about 4 percent KOH-soluble extract at 260° to 280° C. and about 8 percent upon fusion with potassium hydroxide.

Samples of kukersite were heated with sulfur in sealed tubes at 180° to 200° C. for 2 hours. When the tubes were opened, a strong smell of H_2S was noticed; when the pyridine extract of the heated shale residue was poured into water, grey globules with a smell of freshly vulcanized rubber were precipitated.

Shale powder was treated with 3-percent hydrochloric acid to decompose mineral carbonates and was then oxidized with nitric acid. It was found that the action of the acid depended on its strength, the temperature, and the duration of the reaction. It appeared that the organic material of kukersite may be characterized as bituminous rather than humic.

Samples of kukersite were brominated and chlorinated. The halogenated shales showed a solubility in absolute alcohol of 26 percent compared to only 0.31 percent for untreated shale. The alcohol-soluble extract from chlorinated shale contained a considerable quantity of calcium chloride, and the shale residue retained a greater portion of the original chlorine. It was found that enriched shale (4.5 percent ash) did not react with chlorine as much as did raw shale. Apparently the mineral matter acted catalytically during chlorination. Also, addition and substitution of chlorine proceed simultaneously. The ether extract of chlorinated shale appeared to be a derivative of hydroaromatic hydrocarbons.

The amount of soluble extract obtained by solvent treatment of kukersite ranged from 0.22 percent with chloroform to 2.20 percent with tetrachloroethane. The extraction of kukersite with benzene under pressure at about 250° C. yielded less than 1 percent of an extremely viscous oily substance.

Heat was the most effective agent for the depolymerization of kukersite kerogen. Shale samples were heated to 150° C. in the presence of air and again in the presence of carbon dioxide. The percentage loss of weight due to drying in air was much less than in the presence of carbon dioxide. The results indicated that on drying in air, the powdered shale loses water and a volatile substance, probably the oxides of carbon, up to 80° C. Carbon dioxide was also found to be present in the gases eliminated at the temperature of initial decomposition.

Pulverized shale, heated for 6 hours at 220° C., lost 2.6 percent of its weight; its solubility in carbon disulfide was 2.11 percent. In other tests shale samples were heated at 200° to 208° C. for various periods of time up to 6 hours. The heated shale was then extracted with carbon disulfide. The results showed that the amount of extract was increased by extending the heating period.

Kukersite kerogen was formed from compounds that were resistant to bacteriological decomposition, such as waxes and resins, plus decomposition products of proteins, cellulose, and putrefaction products of undigested organisms. The organic matter of kukersite may be regarded as a highly polymerized resinic substance, mixed with calcium salts of fatty acids. Its empirical formula is similar to those of hydroaromatic compounds and certain aldehyde resins or oxygenated cyclic compounds. It is insoluble in ordinary organic solvents, but can be depolymerized by heat and oxidation. The fact that light oils obtained by hydrogenation of kukersite are identical to oils obtained by retorting suggests that kukersite kerogen is composed of concentric layers or long spiral chains of molecules.

166. KOGERMAN, PAUL N., AND KOPWILLEM, JAAN. Hydrogenation of Estonian Oil Shale and Shale Oil. Jour. Inst. Petrol. Technol., vol. 18, 1932, pp. 833-845.

Kukersite was heated in an atmosphere of hydrogen, nitrogen, or water in three series of experiments. Shale samples were heated at 370° to 410° C. for 2 to 3-1/2 hours in the presence of 106 to 287 kg./sq. cm. pressure of water, nitrogen, or hydrogen. In some experiments 5 percent of iron oxide was added to the shale.

The amount of kerogen liquefied by hydrogenation was not greater than the amount of liquid products obtained by ordinary distillation. On hydrogenation, kukersite absorbed 1.8 weight-percent of hydrogen. Almost no hydrogenation took place below the decomposition point of kerogen, and the lighter decomposition products were mainly hydrogenated. Hydrogenation of the shale prevented coke formation. Heating kukersite or its crude oil at temperatures of 400° to 410 C. under 250 kg./sq. cm. hydrogen pressure produced paraffinic and naphthenic oils of lower boiling points. At higher temperatures and after long-continued heating, the formation of aromatic hydrocarbons was observed.

167. DOWN, A. L. The Analysis of the Kerogen of Oil Shales. Jour. Inst. Petrol., vol. 25, 1939, pp. 230-237.

A method is described whereby 99 percent of the mineral matter of British oil shales was removed by mineral acid treatment. The mineral carbonates were removed with 5 N HCl, iron pyrites were removed by nitric acid (specific gravity 1.12) at room temperature and silicates were removed by HF. The composition of the resulting kerogen concentrate was determined and compared with that of the original sample. Attempts of previous workers to isolate kerogen were surveyed.

168. QUASS, F. W., AND DOWN, A. L. Correspondence. The Analysis of the Kerogen of Oil Shales. Jour. Inst. Petrol., vol. 25, 1939, pp. 813-819.

Comments are given on the method developed by F. W. Quass for reducing the amount of mineral matter present in certain coals and oil shales (torbanites). The method consisted of grinding oil shale with water in a porcelain ball mill in the presence of oil. The oil formed a paste with the carbonaceous material, and a greater portion of the mineral matter remained suspended in the water and was separated. Ultimate analyses of the enriched samples indicated that the percent of carbon was higher, the percent of hydrogen and oxygen was lower, and the ratio of carbon to hydrogen and carbon to oxygen increased in the enriched samples.

169. DOWN, A. L., AND HIMUS, G. W. A Preliminary Study of the Chemical Constitution of Kerogen. Jour. Inst. Petrol. Technol., vol. 27, 1941, pp. 426-445.

Eight oil shales from Kimeridge (England), Ermelo (South Africa), Estonia, Amherst (Burma), Kohat (India), Broxburn Main (Scotland), Middle Dunnet (Scotland), and Pumpherston (Scotland) were oxidized by alkaline potassium permanganate. Carbon-balance oxidation, bulk oxidation, and rate of oxidation tests were made.

The constitutions of some kerogens resemble that of coal as there was definite evidence of a benzenoid structure; however, kerogen is less benzenoid than coal. Other kerogens, notably those of the Estonian algal limestones, showed no evidence of benzenoid structure. There was evidence that certain kerogens contained two types of structures, one comparatively easily oxidized by alkaline potassium permanganate and the other highly resistant to attack.

170. HIMUS, G. W. Oil Shales, Torbanites, Their Allies, and Some of Their Problems. Petroleum (London), vol. 4, 1941, pp. 9-13.

A review was made on the composition of oil shale, the constitution of kerogen, microscopic examination of thin sections of oil shale, and the classification of kerogen rocks. There was evidence that some iron may be associated with the kerogen structure, although most of the mineral matter of oil shale is merely mixed physically with the organic component.

171. NEPPE, S. L. A Technical Study of Transvaal Torbanite. Jour. Inst. Petrol., vol. 27, 1941, pp. 31-65.

There was little difference between the composition of oil obtained from torbanite of different mineral content. It was difficult to concentrate torbanite by physical means as the ash associated with torbanite was mainly inherent. The composition of the ash was quite uniform regardless of the percentage of organic material present in the torbanite.

The same general trends in the evolution of oil, liquor, and gas were noted regardless of the organic content of the torbanite and suggested that the different grades of torbanite were from the same parent substance, but in different stages of deterioration.

172. DULHUNTY, J. A. Notes on Solvent Extraction of Torbanite. Proc. Linnean Soc. New South Wales, vol. 67, Pts. 3-4, 1942, pp. 238-248.

Torbanite was extracted with benzene in a pressure apparatus at temperatures from 300° to 400° C. and for periods of time up to 40 hours. A yield of 4 to 14 percent of the organic material was obtained at temperatures from 300° to 340° C. There was a sudden increase in the formation of soluble products at 360° C. with a decrease at 380° C. Extract yields of about 90 percent were obtained at 400° C., and the same quantity of extract was obtained at 360° C. by longer periods of heating. About 50 percent of the total extractable material was formed during the first half hour of heating (at 360° C. in the presence of 840 p.s.i. of C_6H_6 vapor) after which the rate declined; the last 10 percent required 24 hours.

173. DULHUNTY, J. A. The Action of Solvents on Torbanite and the Nature of Extracted Products. Proc. Roy. Soc. (New South Wales), vol. 76, 1943, pp. 268-274.

Tests were made on torbanite with polar and nonpolar solvents under various conditions. Torbanite undergoes no change when heated below 250° C., but depolymerization of the organic matter, absorption of solvent, and swelling and softening of the torbanite occurred between 250° and 300° C., although no appreciable quantity of soluble product was formed. Between 300° and 350° C. depolymerization continued and more solvent was absorbed, which caused swelling, softening, and partial breakdown of the physical structure of torbanite. The intimate mixture of torbanite and solvent produced a jellylike mass, which could not be filtered. Continued heating between 350° and 400° C. caused the organic matter to dissolve in the solvent and produced a complete breakdown in the physical structure of the torbanite. The extracts consisted largely of heavy paraffin compounds, including waxes.

174. LANIN, V. A., AND PRONINA, M. V. (Organic Substances of Bituminous Shales.) Bull. Acad. Sci., U.R.S.S., Classe Sci. tech., 1944, pp. 745-751.

Samples of Gdov (Estonia) and Volga (Russia) oil shales were oxidized by alkaline permanganate to study the distribution of carbon and the composition of the resulting oxidation products.

Gdov shale was rather stable to oxidation and, after 42 hours 61.2 percent of the organic material remained unoxidized. Five hundred hours were required for complete oxidation, and the oxidation products consisted of CO_2, acetic, oxalic, and succinic acids. The oxidation products from Volga shale consisted of CO_2, acetic, oxalic, succinic, adipic, phthalic, benzenetricarboxylic, benzenetetracarboxylic, and benzenepentacarboxylic acids. The results indicated that Gdov shale is free of humic substances and is of sapropelic origin, while Volga shale is of sapropelic-humic origin.

175. **CANE, R. F.** A Note on the Chemical Constitution of Torbanite Kerogen. Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 412-414.

Torbanite originated in a specific type of colonial algae that flourished during Permian age. Part of this algal tissue or some product of its decomposition produced kerogen. As crude shale oil from New South Wales torbanite contains appreciable amounts of paraffin wax, the substance that produced this wax must have contained long chains of carbon atoms. Paraffin wax has never been produced by the thermal breakdown of other hydrocarbon types. This suggests that kerogen originated from fatty matter present in the algae. The fatty matter, which was a source material for kerogen, was probably similar to the fatty acids found in present-day algae of similar structure.

The degradation of fatty matter to free acids in decaying algae was observed; the first stage in the process was when the algal mass passed the initial decay period. The action of decay raised the temperature of the sapropel and caused polymerization of the partly-freed acids. A tough, semisolid, low-degree polymer similar to the present-day coorongite and the Balkash sapropelite resulted. After the first stage in the polymerization, the rubbery mass became covered with an overburden of sandstone and other rocks, and further polymerization took place until a rigid high polymer was formed.

It is possible that oxygen and, to a less degree, sulfur atoms acted as linking elements between polymer molecules. Sulfur occurred in two forms: One loosely held and giving rise to hydrogen sulfide in the early stages of thermal decomposition and the other giving rise to thiophenes and other heterocyclic compounds. However, the presence of heterocyclic compounds in the oil did not prove that nitrogen and sulfur were present in ring structures in the original kerogen. Nitrogen and sulfur probably originated in the protein matter of the algae and were imprisoned during polymerization.

176. _____. The Chemistry of the Pyrolysis of Torbanite. Australian Chem. Inst. Jour. and Proc., vol. 15, 1948, pp. 62-68.

Vacuum heating of torbanite was carried out to establish the lowest temperature at which decomposition could be detected. Slight vapors appeared at 131° C., vapor of pH2 from 200° to 275° C., and oil and H_2S from 327° to 336° C. A quantity of bitumen was prepared by heating rich torbanite for extended periods at about 300° C. The torbanite was then extracted with benzene and a black semisolid residue was obtained. The bitumen was distilled at atmospheric pressure and under vacuum at temperatures of 350° to 400° C.

As the kerogen was heated, slight oxidation took place followed by initial decomposition, which caused loss of sulfur, hydrogen, and oxygen, and the disappearance of some cross-linkages. The result of these reactions was a general softening of the kerogen, accompanied by evolution of hydrogen sulfide and carbon dioxide. As the reaction proceeded, cross-linkages were progressively ruptured until a stage was reached where the macromolecule no longer existed and the structure was essentially elastomeric. In the next stage a few remaining cross-linkages disappeared, and at the same time some sidechains broke away from the parent ring. This heterogeneous mixture constituted the bitumen. From this stage on, no plan was followed, and cracking occurred in the normal manner, producing oil, gas, and carbonaceous residue.

Kerogen decomposition may be represented by: kerogen → bitumen → oil → naphtha + gas + coke. The decomposition appeared to be a cracking reaction, and the formation of bitumen was not due entirely to depolymerization, as the carbon-hydrogen ratio of the reactants and products remain unchanged in a true depolymerization. In the original kerogen, the molecules consist of many units, each containing one or more cyclic nuclei possessing long sidechains. The occurrence of paraffin wax in the crude oil leaves no doubt that long-chain paraffin structures are present, as such, in the kerogen molecule.

177. DANCY, T. E., AND GIEDROYC, V. Further Researches on the Determination of the Chemical Composition of Oil Shales. Jour. Inst. Petrol., vol. 36, 1950, pp. 593-603.

The removal of mineral matter from Ermelo (South Africa) torbanite, St. Hilaire (France) oil shale, and Kimmeridge (Dorset) oil shale was studied by a chemical and a physical method. Hydrochloric acid extracted a small portion of the kerogen from these shales in the form of organic bases; otherwise, acid treatment did not apparently attack the kerogen itself. Boiling with sodium carbonate solution should be avoided since alkali-soluble materials may be formed by oxidation during the treatment. Treatment with zinc and hydrochloric acid did not remove pyrite quantitatively, and nitric acid destruction of pyrite should not be used since the kerogen of oil shale is often nitrated by this treatment. The composition of the kerogen could be determined after an estimation was made of pyritic iron in the ash. Physical removal of mineral matter, where applicable, with graphical presentation of results was the most satisfactory method for determining the true percentage of carbon and hydrogen in the kerogen.

178. _____. Further Investigation of the Chemical Constitution of the Kerogen of Oil Shales. Jour. Inst. Petrol., vol. 36, 1950, pp. 607-623.

The chemical constitution of Ermelo (South Africa), St. Hilaire (France), and Kimmeridge (Dorset) oil shales, using oxidation as a means of degradation, was studied with emphasis on the use of gaseous oxygen and hydrogen peroxide as oxidizing agents. Prolonged oxidation with gaseous oxygen rendered the kerogen soluble in alkali, and there was no indication that oxidation of any particular part took place preferentially. After 120 hours of oxidation, 34.2 percent Ermelo oil shale remained unoxidized by alkaline permanganate. The organic residue from this oxidation yielded nearly twice the amount of oil per gram of carbon as the original shale, indicating that this residue consisted of almost pure and essentially unchanged algal remains. The oil from oxygen-oxidation residues of Ermelo shale showed a decrease in yield of 40 percent and an increase in carbon-hydrogen ratio from 11.0 to 13.0. It may be concluded that gaseous oxidation had a profound effect on the kerogen.

Hydrogen peroxide oxidation of Kimmeridge shale was suitable for the preparation of a range of products from highly complex regenerated humic acids to somewhat similar noncrystalline alcohol- and water-soluble acids. The presence of benzenoid acids established the existence of benzenoid structures in the oil shale; however, there was evidence that an aliphatic structure predominated. Infrared absorption spectra of intermediate acids from the hydrogen peroxide oxidations showed the presence of aliphatic unsaturation (especially conjugated dienes); therefore, the original Kimmeridge kerogen should be even more unsaturated. This may account for the ease by which the kerogen was oxidized and also the tendency of the intermediate acids to polymerize.

The Ermelo torbanite contained algal material plus a humic material, basically benzenoid in structure. The St. Hilaire kerogen also consisted of two distinct types of material similar to that of Ermelo torbanite, but they were probably more condensed with fewer side chains. Kimmeridge kerogen was peculiar in its ease of oxidation and high sulfur content. It seemed to contain mainly unsaturated aliphatic or cyclic structures with a small amount of benzenoid substances. The origin of the sulfur is unknown, but it occurs in the main kerogen structure in a stable combination--possibly replacing oxygen.

179. KOGERMAN, P. N. (Shale Kerogen as a Macromolecular Substance, and the Origin of Shales.) Khimiya i Genezis Tverd. Goryuch. Iskopaemykh, Trudy i Vsesoyuz. Soveschaniya, Moskva, 1950, pp. 368-375.

Ideas and general laws concerning the chemistry of high polymers were used to study the organic matter of oil shale (Estonian kukersite).

The insolubility of kerogen in water, alkali, acids, or organic solvents is similar to two or three dimensional polymers. In an aqueous solution of chloral hydrate, kerogen swells to a certain extent but does not dissolve. This is similar to high polymers. The softening point of kerogen is between 340° and 380° C., at which temperature it acquires plastic properties and resembles high-molecular-weight thermoplastics. Kerogen does not distill without decomposition even at reduced pressures and consequently must have a molecular weight above 1,000. Thermal decomposition products of kerogen are mixtures of low-molecular-weight compounds, the composition of which gives little information concerning the original kerogen. Starch, proteins, lignins, and other natural products give similar materials. The average specific gravity of kukersite kerogen is 1.08 and corresponds approximately to that of polymeric hydrocarbons, cellulose ethers, and natural resins such as copal, sandarac, and others. From these facts, kerogen can be considered to be a high-polymeric substance.

Most modern geologists hold that marine deposits of microscopic blue-green algae are the parent substances of kerogen. However, other plankton organisms, especially diatoms, may have contributed to the organic material present in kukersite. Modern blue-green algae contain 60 percent proteins, 3 percent fat, 5 percent pentosan, 1 percent cellulose, and 31 percent other carbohydrates.

Of all possible methods of destruction or transformation of proteins to kerogen under the conditions of ooze formation and sedimentation, the hydrolysis of proteins to diketopiperazines and amino acids seems most probable. New high polymers were not formed directly from these monomers by polycondensation; otherwise, the nitrogen content of the kerogen would correspond to that of the original material. The amino acid may have split out ammonia ions by the action of bases to form an ion radical that yielded hydroxy acids on hydration. The resulting acids were polycondensed to form linear polyesters and also cyclic six-membered lactides. In another stage of transformation carbon dioxide was evolved by intramolecular decarboxylation with the formation of a carbon chain polymer.

Chemical studies of kerogen, such as halogenation, nitration, permanganate oxidation, and others indicate that kerogen contains both carbon-chain and hetero-chain compounds. The former may have originated from the nonnitrogenous compounds present in the parent blue-green algae, preserved by adsorption on the inorganic portion of kukersite.

180. KARAVAEV, N. M., AND VENER, I. M. (The Godovsk Shale Bitumen.) Khimiya i Genezis Tverd. Goryuch. Iskopaemykh, Trudy i Vsesoyuz. Soveschaniya. Moskva, 1950, pp. 376-385; Chem. Abs., vol. 49, 1955, p. 2266.

Bitumen from Godovsk shale is a high-molecular-weight material containing phenolic, ketonic, and pyridine groupings. When treated with anhydrous aluminum chloride, alkali-soluble products containing phenols were formed. Acid hydrolysis of the bitumen with dilute H_2SO_4 and HCl resulted in the formation of phenols with an average composition of $C_{10}H_{14}O$. Oxidation with alkaline $KMnO_4$ produced only fatty acids and no benzene carboxylic acids. Regardless of the large number of hydroxyl groups present in the bitumen, almost no water was formed during pyrolysis. This indicated the absence of alcoholic hydroxyl groups. The formation of pyridines and phenols during acid hydrolysis indicates the existence of phenol and pyridine groups in the shale. Oxygen is present in forms other than carboxyl, carbonyl, and hydroxyl groups.

181. RAUDSEPP, KH. T. (A New Method of Investigation of the Chemical Structure of Combustible Minerals, and the Chemical Structure of the Estonian Shale-Kukersite.) Izvest. Akad. Nauk S.S.S.R. Otdel. Tekh. Nauk, No. 3, 1954, pp. 130-136.

Finely ground Estonian kukersite was concentrated by treatment with a 3-percent solution of acetic acid followed by centrifuging in a solution of calcium chloride (specific gravity 1.3). The product (yield of 90 percent) contained 5 to 11 percent mineral components. The shale was treated with hydriodic acid (specific gravity 1.87 and 1.98) at temperatures of 175° to 200° C., and for periods of time up to 72 hours. The resulting products were tested for free iodine, which was equivalent to the amount of hydrogen consumed in the process of reduction. On treating the kerogen with superconcentrated hydriodic acid, the oxygen bonds in the kerogen split and produced low-molecular-weight products that were soluble in ether or benzene.

It was concluded that the macromolecules of kerogen consist of aromatic nuclei and aliphatic hydrocarbon chains, connected among themselves in three-dimensional structures by ether bonds. Other complex-ether bonds are present in certain amounts, mainly in the peripheral part of the macromolecule. The benzene nucleus has a phenolic-ether character and is connected to the neighbor by aliphatic chains and ether linkages.

182. **AARNA, A. YA.** (Isothermal Decomposition of Baltic Oil Shale.) Zhur. Priklad. Khim., vol. 28, 1955, pp. 1138-1142; Chem. Abs., vol. 50, 1956, p. 1293.

Heating oil shale at 300° to 440° C. yields a primary tar. Longer heating, regardless of temperature, results in the formation of heavier tar fractions. Higher temperatures tend to increase the middle and high-boiling fractions and to increase the concentration of unsaturated hydrocarbons at the expense of saturated hydrocarbons. Phenols appear, even at lower heating temperatures, indicating that aromatic structures are present or generated during the process.

183. **FOMINA, A. S., AND POBUL, L. YA.** (The Separation and Identification of Saturated Dibasic Acids. III. Oxidative Degradation of Kukersite Kerogen.) Izvest. Akad. Nauk. Estonian S.S.R., vol. 4, No. 1, 1955, pp. 48-56.

Partial oxidation of 50 percent of the organic carbon in kukersite with alkaline potassium permanganate resulted in the formation of steam-volatile monobasic acids, oxalic, and other dibasic acids. The oxidation products were separated on a column of silicic acid. Succinic, glutaric, adipic, pimelic, suberic, and azelaic acids were identified. The unidentified higher molecular-weight acids were assumed to be formed by partial oxidation of naphthenic derivatives, hydroxy acid polymers, aldehyde acids, dihydric alcohols, etc. The major part of the kerogen was considered to be definitely nonaromatic in character.

184. **AARNA, A. YA., AND KASK, K. A.** (Properties of Pyrobitumens From Baltic Combustible Shale.) Zhur. Priklad. Khim., vol. 29, 1956, pp. 764-768; Chem. Abs., vol. 50, 1956, p. 16076.

Pyrobitumen produced from Estonian shale by heating at temperatures of 300° to 400° C. was studied. The molecular weight of the benzene-soluble extract decreased from 1,300 to 480 as the temperature was increased from 300° to 400° C. Extracts treated with 70 percent HI in sealed tubes at 170° to 178° C. for 40 hours (conditions not likely to rupture carbon to carbon bonds) gave materials whose molecular weights ranged from 400 to 600. It appeared that the soluble bitumen was an intermediate product of kerogen decomposition and that the structural units in the pyrolytic bitumen are linked by oxygen bridges. Extensive pyrolysis ruptures the oxygen bridges and leads to bitumen of lower molecular weight.

185. **KOLLEROV, D. K.** (The Rate of the Thermal Decomposition of the Organic Substances of Oil Shales.) Khim. i Tekhnol. Topliva, 1956, No. 10, 1956, pp. 55-62; Chem. Abs., vol. 51, 1957, p. 5392.

Thermal decomposition of solid fuels (oil shales as well as coals) takes place in two stages. The first stage is depolymerization of the organic material into plastic fluids by a process called bituminization. The second is the pyrolysis of the bitumen into tar, gas, and carbon residue.

186. KASATOCHKIN, V. I., AND ZILBERBRAND, O. I. (Chemical Structure of Shale Kerogen.) Doklady Akad. Nauk S.S.S.R. 111, 1956, pp. 1031-1034.

Samples of kerogen concentrate prepared by leaching Estonian and Volga oil shales with HCl and HF acids were analyzed by X-ray diffraction and infrared spectra. Kerogen is a macromolecular substance with absorption at 6.25 and 6.65 microns, typical of aromatic substances. Condensed aromatic rings seemed to be absent. Only a very small number of methyl groups were present, and none of these were at the end of chains. There was evidence of CH_2, COOH, C=O, and C-O groupings. The kerogen structure consists of aromatic rings with aliphatic sidechains composed of methylene groups plus considerable oxygen and possibly other heteroatoms.

187. AARNA, A. YA., AND LIPPMAA, E. T. (Cleavage of Ether Bonds in Kerogen From Estonian Oil Shale.) Zhur. Priklad. Khim., vol. 30, 1957, pp. 312-315.

The nature and number of ether bonds in kerogen were studied. A 95.4 percent kerogen concentrate was prepared by centrifuging pulverized shale in calcium chloride solutions and removing mineral carbonates by acetic acid. Preliminary treatment of kerogen with boron trichloride, stannic chloride, anhydrous aluminum chloride, anhydrous aluminum bromide in pyridine and metallic sodium in liquid ammonia showed that anhydrous aluminum bromide was the most effective reagent to cleave ether bonds. The results of these tests indicate that the oxygen structures in Estonian oil-shale kerogen have the following distribution: 1.3 percent carboxyl, 29.4 percent hydroxyl, 13.3 percent carbonyl, 16.0 percent phenol ester, and 40.0 percent phenol ether groups.

188. _____. (Structure of the Carbon Skeleton of Estonian Shale Kerogen.) Zhur. Priklad. Khim., vol. 39, 1957, pp. 419-426.

Methods for direct chemical determination of aromatic-ring content of kerogen in Estonian oil shale are given and include the following: (1) Coupling with diazonium salts, (2) chloromethylation of kerogen, and (3) addition of mercuric acetate to kerogen. A kerogen concentrate, obtained by centrifuging from a solution of calcium chloride, was used for the experiments.

Estonian kerogen did not couple with p-nitrobenzenediazonium chloride, which indicated the absence of phenolic hydroxyl group and enols. Coupling with 2,4,6-trinitrobenzenediazonium sulfate or p-diazobenzenediazonium sulfate showed the presence of 0.14 equivalents of aromatic rings per 100 grams of organic matter. Chloromethylation of kerogen with paraformaldehyde and concentrated hydrochloric acid showed the presence of 0.16 equivalents of aromatic rings per 100 grams of organic matter. Reaction between the kerogen and mercuric acetate proceeded readily and indicated the presence of 0.23 equivalents of aromatic rings per 100 grams of kerogen. The most probable content of aromatic rings in kerogen is 0.2 equivalents per 100 grams of kerogen, which corresponds to 19 percent of the total carbon based on absence of condensed rings. The carbon distribution of kerogen may consist of 19 percent carbon in aromatic rings, 50 to 75 percent in naphthenic rings, and 6 to 31 percent in paraffin chains.

189. KINNEY, C. R., AND SCHWARTZ, DONALD. Partial Air Oxidation of Chattanooga Uraniferous Black Shale. Ind. Eng. Chem., vol. 49, 1957, pp. 1125-1130.

The organic matter in Chattanooga (United States) shale appears to be different from that in other oil shales. The material has a low atomic hydrogen-carbon ratio and a high percentage of oxygen. The low ratio of hydrogen to carbon suggests that a large part of the carbon structure is of an unsaturated polycyclic or aromatic nature. Many of the oxygen groups appeared to be alcoholic in character, but ether linkages and phenolic groups may also exist. Partial oxidation destroys the alcoholic groups with the introduction of carboxyl groups. These acids appeared to be mainly quinoid in nature as determined from ultimate analyses, equivalent and molecular weights, infrared absorption characteristics and behavior on oxidation with alkaline permanganate. The presence of large amounts of silicon, aluminum, iron, titanium, magnesium, calcium, and sodium in these acids indicates the presence of metal complexes.

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NOTES ON UNPUBLISHED BUREAU OF MINES RESEARCH, 1946-57

I. Theories of Origin

Dried sea-floor sediments from Catalina basin off the California coast were composited for analysis, and an organic concentrate was prepared from the composite sample by treatment with hydrochloric and hydrofluoric acids. The composition of the organic material in the sea-floor sediment differed from that of Colorado oil-shale kerogen by a much higher carbon-to-hydrogen ratio and a higher percentage of nitrogen, sulfur, and oxygen. The retorted oils were also different as the oil from the sea-floor sediment showed lower hydrogen content and higher nitrogen, sulfur, and oxygen contents. The nitrogen content of 4.2 percent suggested that animal tissue (protein) was the source of the sea-floor organic material. Although it may be possible that organic material similar to that found in the sea-floor sediment is the precursor of oil-shale kerogen, considerable alteration would be necessary to form kerogen.

II. Petrographic Characteristics

Microscopic examination of thin sections of Colorado oil shale assaying 73 gallons of oil per ton showed the formation of liquid oil and darkening of the yellow organic material at 200° to 205° C. The color of the latter gradually changed to light red, then finally to dark cherry red at 250° C. At the maximum temperature attainable by the hot stage of 350° C., all the organic material turned black. (Some black organic material was in the original sample.) A thin section previously extracted with benzene was treated similarly. The same changes occurred except that formation of the initial oil was not observed. This indicated that, in the first test, the oil was derived from the benzene-soluble material.

Oil shale from Rifle (Colo.) was crushed to pass a 100-mesh-per-inch screen, and the organic particles were measured microscopically. On the average, the organic particles were larger than the mineral particles: Organic material 0.125 mm., siliceous minerals 0.037 mm., and calcareous minerals 0.006 mm.

III. Composition

Ultimate analyses of the organic constituents were determined for three oil-shale samples assaying 21 to 28 gallons of oil per ton from Naval test hole E in Garfield County, Colo. One sample was from a bed 255 to 260 feet above the Mahogany marker, one from 240 to 245 feet below, and the third was 685 to 690 feet below the marker. Although these samples were from beds up to 950 feet apart, the ultimate compositions of their organic constituents were very similar.

Other samples of Colorado oil shale were oxidized with 30-percent hydrogen peroxide for 6 hours at room temperature. By this treatment, the original organic carbon content of 26 percent was reduced to 3 percent and corresponded with the amount of residual carbon normally obtained with other oxidants. Minerals present in the shale were partly altered by the oxidation; pyrite and organic sulfur were oxidized to sulfate ions, and the soluble filtrate contained sodium, magnesium, and calcium ions.

IV. Method of Concentrating Kerogen

Enriched kerogens prepared by treating Colorado oil shale with concentrated hydrochloric (HCl) acid or a mixture of HCl plus hydrofluoric (HF) acids contained 0.7 to about 3.3 percent chlorine and small but unknown amounts of fluorine.

Extraction of mineral matter in oil shale from Rifle (Colo.) by ethylenediaminetetraacetic acid (EDTA) was studied by treating raw shale with a 20-percent solution of EDTA in ammonia water for 24 hours. The EDTA chelated with calcium, magnesium, and iron (essentially the same elements removed by dilute acetic acid treatment). The major mineral components—quartz, feldspar, illite, and pyrite—were not chelated.

Samples of pulverized oil shale from Rifle (Colo.) were treated with sonic energy by the Raytheon Manufacturing Co. Some of the samples had been previously leached with dilute acetic acid to remove mineral carbonates. Based upon ash content, the sonic treatment caused little separation of the organic and inorganic constituents.

V. Reaction of Heat

Enriched Colorado oil shale showed no increase in weight owing to oxidation by drying at room temperature for 7 days. Oven drying in air at 105° C. caused a loss in weight during the first 2 hours and a slow gain in weight thereafter. Treatment of an organic concentrate containing 33.8 percent ash with oxygen at 150 p.s.i.g. and 100° C. for 24 hours caused a weight gain of 5.58 percent. Sixty-five percent of this added oxygen was recovered as water by heating the sample to 550° C. The following yields of water, based on organic matter, were obtained in a similar manner from the following samples: (1) Raw shale, 2.1 percent; (2) raw shale extracted with benzene and treated with acetic acid, 2.7 percent; (3) the sink fraction from item 2, 3.0 percent; and (4) the sink fraction from item 3 after treatment with hydrochloric and hydrofluoric acids, 3.6 percent. The increase in water yield indicated oxidation of organic material by the enrichment treatments.

Calculations were made to determine the distribution of the elemental components that appeared in the pyrolytic products obtained from kerogen. This was made from published data on Colorado oil shale. Organic carbon in kerogen was distributed in the pyrolytic products as follows: 1 percent as CO_2 and CO, 4 percent as hydrocarbon gases, 45 percent as nonhydrocarbon material, 22 percent as nonparaffinic hydrocarbons, 8 percent as paraffin hydrocarbons, and 20 percent as carbon residue. Sixty percent of the kerogen oxygen was removed as water, 28 percent as CO_2 and CO, and 12 percent remained in the oil. Of the total hydrogen accounted for, 61 percent remained in the oil, 24 percent was removed as gases (mostly hydrogen gas), 5 percent as pyrolytic water, and 9 percent remained on the spent shale. Fifty-four percent of the nitrogen was in the oil, 8 percent was removed as gas, and 38 percent remained on the spent shale. Thirty-three percent of the sulfur was removed as gases, and 67 percent was in the oil.

Colorado oil shale was retorted at 500° C. in a large Fischer retort under reduced pressures of 1.8 to 40 mm. mercury, while flushing with carbon dioxide or with air. Retorting at reduced pressures produced lower yields of water but slightly higher yields of oil having increased specific gravity and viscosity. Retorting at atmospheric pressure without a flushing gas or by flushing with carbon dioxide yielded oils of lower gravity. Flushing with air caused some oxidation as indicated by an increase in the yield of water and decrease in the specific gravity of the oil. However, tar-base and tar-acid determinations did not indicate marked differences in the oil.

Samples of raw oil shale from Rifle (Colo.) and samples of raw shale that had been previously leached with 10 percent HCl acid were assayed by the modified Fischer retort method to determine the effect of acid leaching on the production of assay water. Each sample produced water that was visible in the collecting tube. However, after centrifuging, water could not be seen in the distillate obtained from acid-treated shale. This was attributed to the dissolving of hydrophillic tar in the water layer. Excess oil was removed by solvents, and the amount of water was determined by Dean-Stark distillation. Since the water layer after centrifuging could be distinguished only by removing the oil with solvents, errors might possibly be made in the percent of assay water obtained from HCl enriched shale by the modified Fischer retort method.

VI. Physical Properties

Samples of enriched kerogen containing 13.8 percent ash were exposed to oxygen at atmospheric pressure and at a pressure of 25 atmospheres for 24 hours. Presumably owing to oxidation, the sample exposed to the atmosphere at 110° C. gained 0.13 percent in weight. About the same gain in weight was obtained under pressure at 25° C., but an 8.44 percent gain in weight was obtained by the use of pressure at 110° C. Benzene-soluble material from oil shale did not gain in weight under these conditions.

VII. Soluble Kerogen

Colorado oil shale was extracted in a Soxhlet-type extractor with different solvents at their boiling points. The oil shale had been previously extracted with benzene (1.7 percent of soluble material was removed) and leached with dilute acetic acid to remove mineral carbonates. The yields of soluble kerogen from the treated shale were determined by the weight of the extract or the loss in weight of the shale sample. The boiling points of the solvents and the yields of extracts in weight-percent of the shale were as follows: Ethylene chloride (75° C.), 2.4 percent; pyridine (106° C.), 5.1 percent; ethylene diamine (110° C.), 4.9 percent; dimethylformamide (114° C.), 5.8 percent; tetralin (196° C.), 24 percent; o-cyclohexylphenol (270° C.), 1.8 percent; and phenanthrene (340° C.), 18 percent.

Colorado oil shale was extracted with various solvents under different conditions. Extraction conditions and yields of extracts in weight-percent of kerogen follow: (a) Soxhlet extraction at atmospheric pressure for 168 hours: Acetone (49° C.), 6.8 percent; chloroform (54° C.), 9.3 percent; toluene (93° C.), 11.0 percent; tetrachloroethylene (93° C.), 11.5 percent; and xylene (121° C.), 11.3 percent. (b) Soxhlet extractions at atmospheric pressure for 150 hours: biphenyl (193° C.), 15.0 percent; phenol (160° C.), 18.4 percent; and catechol (185° C.), 16.4 percent. (c) Extraction with benzene at atmospheric pressure and at 65.6° C.: 1 hour, 8 percent; 2 hours, 13 percent; 4 hours, 13 percent; 8 hours, 14 percent; 24 hours, 14 percent; 50 hours, 15 percent; 100 hours, 16 percent; 168 hours, 15 percent; and 217 hours, 15 percent. (d) Extraction with benzene in the presence of a gas comprised of 3 parts hydrogen and 2 parts carbon dioxide at autogenous pressure: 6 hours at 177° C., 14.8 percent; 335 hours at 204° C., 17.7 percent; 6 hours at 260° C., 15.1 percent; 85 hours at 260° C., 22.2 percent; 200 hours at 260° C., 27.7 percent; 500 hours at 260° C., 30.3 percent; and ultimate solubility in benzene at 260° C. (based on graph), 31.4 percent.

When oil shale was extracted under pressure with benzene at 177° C. for 260 hours, 0.5 percent of the kerogen was liberated as carbon dioxide. This indicated decarboxylation of kerogen. However, a fixed amount of organic material in oil shale was soluble without decomposition. The rate of decomposition of the organic material at 177° C. and below was negligible. From 177° C. to 260° C., the rate of decomposition, as measured by increase in solubility, became appreciable and increased with rise in temperature.

Oil shale from Rifle (Colo.) was extracted for 30 minutes by various solvents at 200° C. in a pressure reaction vessel. Percentages of extracts obtained from kerogen were: Acetone 5.3, n-heptane 6.1, methyl alcohol 8.0, benzene 8.5, phenol 15.5, and tetralin 27.8. Nitrogen structures in kerogen were quite insoluble and none of the extracts contained a higher atomic ratio of nitrogen to carbon than the kerogen. The methyl alcohol extract had the highest nitrogen content and equaled only 40 percent as much as the kerogen. Of all the extracts, only the methyl alcohol extract contained more sulfur and oxygen per carbon atom than the original kerogen (10 percent more sulfur and 110 percent more oxygen). Extracts obtained by n-heptane, methyl alcohol, benzene, and acetone contained more hydrogen per carbon atom than the original kerogen; the n-heptane extract was the highest and contained 1.1 times the amount of hydrogen in the original kerogen.

Fifty-gram batches of Colorado oil shale were extracted with 200 milliliters (ml.) of a trona solution consisting of equal parts of 5-percent solutions of sodium carbonate and sodium bicarbonate until a total of 1 kilogram of shale had been treated. The treatment yielded a dark-colored extract with a distinct odor. Acidification of the extract precipitated brown organic acids amounting to 0.08 percent of the shale, but the greater portion of the organic acids remained soluble in the acid solution. The precipitated acids were tacky at room temperature and were more soluble in organic solvents than those derived from the trona brine in the Green River formation of McDermott field, Sweetwater County, Wyo.

Samples of benzene-soluble material, which were extracted from rich Colorado oil shale, were heated in the absence of oxygen for 22 hours at 200° C. and 38 minutes at 475° C. Twenty percent of the material was volatilized at 200° C., and 96.6 percent was volatilized at 475° C. The residue, which amounted to 3.4 percent of the starting material, was not soluble in benzene.

VIII. Degradation Studies

Samples of precipitated kerogen acids (regenerated humic acids) were heated for 1 to 480 hours at 200° C. in an atmosphere of nitrogen. The heated material was extracted with benzene to remove soluble oil and was pyrolyzed at

500° C. The amount of benzene-soluble oil formed then was determined. Carbon dioxide evolution from the acids was continuous for 480 hours and increased from 2.5 weight percent after 5 hours' heating at 200° C. to 4.4 percent after 480 hours' heating. Water increased from 3.1 percent after 5 hours' heating to 10.5 percent after 480 hours' heating. Oil obtained by pyrolysis of the heated residue at 500° C. was 32.8 percent after 5 hours' heating and 32.5 after 480 hours; however, benzene-soluble oil from the material heated at 200° C. decreased from 5.9 percent after five hours to 1.8 percent for 480 hours' heating. The acids became insoluble in 5 percent alkali after 5 hours' heating, indicating that carboxyl groups had been removed. At this point, 57 percent of the total carbon dioxide formed by 480 hours' heating had been evolved from carboxyl groups. The remaining 43 percent appeared to come from other structures in the acids. It also appeared that the precipitated acids were readily decarboxylated and dehydrated. The initial decarboxylation began at approximately 150° C.

The total methoxy and ethoxy contents of the precipitated kerogen acids derived from Colorado oil shale ranged from 0.3 to 3.5 weight-percent.

Kerogen acids were decarboxylated by the copper-quinoline method by heating 100-g. samples with 35 g. of anhydrous cupric sulfate in 350 g. of fresh distilled quinoline for 24 hours at 125° C., plus an additional 7 days at 225° C. The volatile material was collected in a dry ice-acetone bath. The residue was washed free of quinoline and was recovered. The small amount of volatile material (less than 5 g.) consisted of 1-butanol, 2-butanol, 2-methyl-2-propanol, 2-methyl-2-butanol, sulfur dioxide, carbon dioxide, hydrogen sulfide, and some butenes. The remainder of the product consisted of a high-molecular-weight material insoluble in benzene but soluble in acetone, plus an insoluble carbon residue.

Samples of raw shale from Rifle (Colo.) were oxidized by oxygen at 275° C. for 12 to 48 hours by charging oil shale into a pressure vessel along with an aqueous solution of KOH and 1,000 p.s.i.g. of oxygen. The results showed that 83.0 percent of the kerogen was oxidized after 12 hours, 84.8 percent after 24 hours, 88.3 percent after 36 hours, and 95.6 percent after 48 hours. The usual oxidation products were formed; namely, carbon dioxide, volatile acids, and nonvolatile acids.

Pyrolytic products from oil-shale kerogen from Rifle (Colo.) were oxidized by alkaline potassium permanganate for 100 hours to determine if their oxidation behavior was the same as that of kerogen. Five different fractions, namely N-T-U crude oil, N-T-U heavy gas oil, N-T-U wax, N-T-U crude-oil residuum, and kerogen were oxidized, and the distribution of carbon in the oxidation products was determined. Twenty-six percent of the N-T-U crude oil, 43 percent of the heavy gas oil, 63 percent of the wax, 7 percent of the residuum, and 1 percent of the kerogen remained unoxidized after 100 hours. Thirty-three percent of the kerogen was oxidized to oxalic acids compared with less than 5 percent of the other products. Only 4 percent of the wax was oxidized to carbon dioxide compared with 50 to 86 percent for the other products. The oxidation behavior of kerogen was different from that of its pyrolytic products. This indicated the pyrolysis altered kerogen and made the resulting material more resistant to oxidation.

Organic acids, precipitated from natural trona brine of the Green River formation in McDermott Basin (Wyo.), were studied. They resembled kerogen from Colorado oil shale in general appearance and some properties. By heating, the acids started to fuse at 120° C. and gradually formed a resinous mass, but no decomposition was observed up to 170° C. Swelling, foaming, and coking occurred during assay that yielded 73.3 percent of oil (182 gallons of oil per ton), 3.8 percent water, 7.8 percent gas, and 15.1 percent of carbonaceous residue. The assay oil from the trona acids resembled shale oil, except for slightly higher specific gravity (0.964), higher oxygen and sulfur contents, and contained less basic constituents. The neutral portion of one oil fraction contained about the same types and amounts of hydrocarbon as those in shale oil; however, another fraction had more paraffins and cycloparaffins but less olefins than the corresponding fractions from shale oil. The assay gas from the trona acids resembled that from shale, except it contained 11 times as much carbon monoxide and only one-eighth as much hydrogen (CO_2 was about the same). The trona acids had molecular weights of about 1,450, and infrared spectra indicated the presence of carboxyl and aliphatic groups. Treatment with nitric acid under conditions favoring nitration of aromatic structures caused little reaction, but conditions favoring nitration of paraffins caused extensive reaction. Fifty parts of trona acids dissolved in 100 parts of alkalies, but only small amounts were soluble in organic solvents. Moreover, the dried acids dissolved more slowly in aqueous solutions than did the freshly precipitated material. Neutral equivalents indicated the acids contained three acidic groups. Based on silver salts, the acidic groups consisted of two carboxyl groups and one acid hydroxyl group per molecule and accounted for about one-half the available oxygen.

Various hydrolytic, oxidative, and pyrolytic tests were performed on oil shale from Rifle, Colo. Samples of oil shale were degraded by solutions of 20 percent potassium hydroxide, 10 percent alcoholic potassium hydroxide, 30 percent hydrochloric acid, and by oxidation with 60 percent nitric acid; also, by fusion with solid potassium hydroxide, by thermal extraction, and by thermal degradation. Approximately 5 percent of the kerogen was degraded by the hydrolytic tests, except for the alcoholic potassium hydroxide that degraded about 20 percent of the kerogen. The following compounds were tentatively identified in the degradation products from various treatments: (1) Alkali treatment--2-ethylhexanol, acetic acid, isobutyric acid, butyric acid, alpha-hydroxy isobutyric acid, isovaleric acid, 3,4-dihydroxy-benzoic acid, alkylpyridine compounds, pyrrolidine, morpholine, porphyrin products, and vanillin. (2) Hydrochloric acid treatment--d-glucose, d-galactose, dl-pinocampheol, alpha-terpinol, terpineol-4, ethanethiol, furan-2-carboxylic acid, and 5-methyl-furan-2-carboxylic acid. (3) Nitric acid treatment--butyric acid, alpha-hydroxy isobutyric acid, isovaleric acid, bb'-dimethyl acrylic acid, cyclohexanecarboxylic acid, p-dodecahydrodiphenic acid, alkylcyclohexene carboxylic acid, cyclohexenealkylcarboxylic acid mixture, umbelliferone, alpha-alkyldecalin, and p-menthane. (4) Thermal solution and pyrolysis--pyrrole, 2-methylpyridine, 4-methylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, 1,2-dimethyl-4-pentylbenzene, o-cresol, p-cresol, furfural, and dipentene.

The identification of low-molecular-weight terpene products and polyisoprenoid and hydroisoprenoid products in degradation products indicated the presence of carotenoid-type structures in kerogen. Distillation products from kerogen appeared to be similar to those obtained from copal resin. The carbohydrate-type humin product, recovered from the acid hydrolysis of kerogen, indicated the presence of carbohydrate derivatives. The presence of intramolecular and intermolecular linkages was indicated by the isolation of anhydrides, lactones, carbimides, and esters. A significant amount of the kerogen appeared to contain carboxyl groups combined with alkaline earth-metal ions.

A sample of enriched oil shale from Rifle, Colo., was reduced by heating the sample at 200° C. for 24 hours in the presence of hydriodic acid (specific gravity 1.96). By this treatment, 14.1 percent of the kerogen was made soluble in ether and benzene. Comparable tests on Estonian oil shale made 93.0 percent of the kerogen soluble.

Raw oil shale was extracted with ethylene carbonate and propylene carbonate at 200° C. for one-half hour. Ethylene carbonate extracted 25.5 percent of the kerogen, and propylene carbonate extracted 9.0 percent kerogen based upon the weight of extract. On the basis of ash-to-kerogen ratio, the propylene carbonate extracted 8.6 percent kerogen. Researchers could not determine the percent extracted by ethylene carbonate on the basis of ash to kerogen ratio as the shale sample gained 6 percent in weight during the extraction. This indicated that ethylene carbonate reacted with the oil shale in some manner.

Dehydrogenation of Colorado kerogen was attempted by treatment with sulfur in boiling solutions of alpha-methyl naphthalene and phenanthrene, and also by treatment with selenium in boiling phenanthrene. By the sulfur treatment, kerogen was carbonized, and the solvents were partly degraded. No additional kerogen was converted to a soluble form by these dehydrogenation treatments.

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U.S. GOVERNMENT PRINTING OFFICE : 1960 O - 553087